

Origins of the thermometer. (Burckhardt, *Die Erfindung des Thermometers und seine Gestaltung in 17 Jahrhundert* (1867).)

# TEMPERATURE MEASUREMENT AND CONTROL

by

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## Preface

Temperature and its control is of fundamental importance in nearly all technical fields. Recognition of the value of this branch of physics in the training of students in physics, chemistry, engineering, metallurgy and ceramics is evident in the inclusion of courses in heat and temperature in the curricula of many universities. In a course in temperature measurement offered to students of diverse interests there is need for a textbook less formidable than the comprehensive treatises on thermodynamics and yet sufficiently general and rigorous to justify its use as a college textbook.

It is the purpose of this book to outline an experimental study of the methods of temperature measurement with the theoretical principles necessary for their appreciation, intelligent use and extension. Many of the advances which have been made in this field since the publication of "Pyrometric Practice" by the National Bureau of Standards (1921) are discussed with illustrations and references to the original papers.

The course of study outlined here is of a practical and specialized nature. Yet it is earnestly hoped that the manner in which the material is presented will aid the student in attaining certain broad objectives which are common to all sciences:

1. Acquisition of information in the field being studied and an understanding of its technical terminology
2. Facility in the clear expression of ideas
3. Skill in laboratory techniques
4. Familiarity with reliable sources of information, and the ability to read scientific work critically
5. Interest in natural phenomena and the ability to recognize unsolved problems
6. Ability to plan experiments and to draw reasonable conclusions from experimental data.

The theoretical basis of temperature measurement is presented in Part I. These chapters are necessarily so compact

that, on first reading, the student's reaction may be merely the query, "So what?" Answers to this pertinent question are suggested in the laboratory experiments of Part II as well as in the numerical exercises.

This book presents the substance of a course offered (for Juniors) by the Physics Department of The Pennsylvania State College. One year of elementary physics is the prerequisite. The course is given in one hour of recitation and a three-hour laboratory period each week for one semester. The experiments have been developed and tested by actual laboratory use over a period of years by an average of a hundred students each year. The present book is a revision of a preliminary edition published under the title "Temperature Measurement" (1941).

To Professor D. C. Duncan and Professor L. T. DeVore, who also have taught the course in Heat and Temperature Measurement, the author expresses his deep gratitude for their helpful criticism of the manuscript.

Grateful acknowledgment is made of the helpfulness of Dr. H. T. Wensel and Dr. H. J. Hoge, of the National Bureau of Standards, for suggestions relating to Chapters 3, 4 and 6; and to Dr. E. F. Mueller and Dr. E. C. Critenden, of the Bureau, for criticising Chapters 7 and 15, respectively.

To the many individuals and instrument manufacturers who have contributed information and illustrations for this book the author is greatly indebted. Particularly helpful has been the cooperation of the Leeds & Northrup Company in editing parts of the text in connection with which the experience of recognized instrument specialists seemed desirable. The sources of illustrations and tables are indicated in the text. Finally, my very special thanks go to J. L. Weber for assistance in the preparation of the manuscript and in the correction of the proofs.

R. L. W.

## Foreword

At some stage in their making, practically all industrial products pass through one or more processes in which temperature is an important factor. Choice of method and instruments to keep the temperature within set limits may have a considerable bearing on product cost and quality, on continuity of production and on life of capital equipment. Consequently, choice is not only of interest to operators, maintenance men, production executives and others directly concerned with a process, but to those responsible for marketing and management. For these reasons, and also because of the need for reliable temperature data in the efficient generation of power, and in the regulation of air-conditioning systems for human comfort or control of a process, a knowledge of the fundamentals of temperature measurement and control should be of practical value to students in all branches of engineering.

In developing methods and instruments to hold an ever-widening variety of manufacturing processes within increasingly-closer temperature limits, industry follows the lead of science. By insisting that the sound principles underlying laboratory measurements be applied in instruments adapted to the rough conditions of plant use, it has advanced, step by step, from the early days of "spit and sizzle" to the modern, automatically-balanced potentiometer pyrometer. Among the first plant instruments were the hand-operated instruments of the laboratory. Their use led to the development of mechanisms to measure and to record temperature automatically. Then, motor-operated control devices . . . regulated by the recorders . . . were developed to adjust heat-input automatically.

Today, when instruments are being selected for a new heat process, or for a modified old one, the above historical development of the pyrometer is, in effect, often paralleled. In the laboratory stage of the development, hand-operated instruments are used to determine critical temperatures. Then, in the pilot plant, where actual plant operations are developed, automatic recorders supply the data which will later form the basis for selection and adjustment of the automatic temperature control system which will be used in the final operating setup.

That industrial instrumentation will continue to follow the lead of science and to proceed from manual to automatic methods, the student need have little doubt. Thermometers of the expansion, pressure and electrical-resistance types; millivoltmeters and potentiometer pyrometers for thermocouple and radiation-type elements are all progressive developments which demonstrate that the laboratory device of today, in some suitable form, will be the industrial device of tomorrow.

In this book, Dr. Weber has treated both the theory and practice of temperature measurements in a way which does credit to the instrument art and makes a distinct contribution to users and prospective users of temperature measuring and controlling instruments.

C. R. CARY,

*Vice-President,*

Leeds & Northrup Company.

*June 23, 1941.*

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## PART I

# Principles Utilized in Temperature Measurements

## CHAPTER I

### Expansion Thermometry

Evolution of Concept of Heat and Temperature.  
Development of Measuring Instruments.

#### Heat and temperature

Heat is a form of energy. A hundred years ago this statement was regarded as a debatable hypothesis. It found verification in the experiments of Joule, Rumford, Davy, Mayer, Helmholtz and Colding in measuring the heat equivalent of mechanical work. This led to the formulation of a conservation of energy principle, explicitly stated by Helmholtz in 1847, which, by gradual extension, has become an implicit part of all theory in the physical sciences. Our concept of heat, as an exact physical term, is defined as "energy that is transferred from one body to another by a thermal process." A thermal process means radiation, conduction, or convection—or a combination of these.

Heat is an *extensive* quantity. It follows the law of addition just as do length and mass.

Our fundamental concept of temperature is obtained from the sensation of warmth or cold which we experience upon touching any object. Such expressions as: ice-cold, cool,



tepid, lukewarm, warm, hot, etc., indicate that our qualitative appreciation of temperature precedes our use of numbers to characterize it. Our experience further tells us that when two similar bodies at different temperatures are placed in thermal communication (and cut off from such communication with all other bodies) the hot body becomes colder and the cold body becomes warmer, until the two reach a thermal state or temperature which, judged by our senses, is the same. However, our idea of what takes place during this equalization of temperature is obtained only after considerable reasoning to generalize a great mass of quantitative data.

Our observation then, plus our concept of heat exchange as an energy transfer, enables us to say that in the equalization of temperature, heat passes from the hotter to the colder body. In seeking for a definition of temperature, therefore, we find it difficult to improve on the one given by Maxwell, which is "The temperature of a body is its thermal state considered with reference to its ability to communicate heat to other bodies."

Of two bodies having different temperatures, the one which communicates heat to the other is said to be at the higher temperature. In devising temperature scales its temperature is customarily, though not necessarily, assigned the greater number.

Suppose we have a body  $A$  which can communicate heat to a body  $B$ , i.e.,  $A$  is at a higher temperature than  $B$ . Experience shows that if a third body, a thermometer, is placed in intimate thermal contact with  $B$  (the colder) and allowed to remain there until all heat transfer between them has ceased, the thermometer, when now placed in contact with  $A$  will, in general, receive heat from the latter. Conversely, if the quantity of heat which a body  $A$  can communicate to a particular thermometer is greater than that which  $B$  can communicate to that same thermometer, then  $A$  will in general be able to communicate heat to  $B$ . When this is not the case certain difficulties must be faced.

If a piece of platinum is placed in a stream of illuminating gas the platinum will get hot even though it and the gas were initially at the same temperature. The platinum will catalyze the combination of the gas with oxygen even at room temperature. In fact gas lighters have been made using this principle. The transfer of energy from the cold gas to the platinum is not a simple thermal process but involves a different kind of process, a chemical reaction. A bare platinum thermocouple or a bare platinum resistance thermometer, therefore, cannot indicate the temperature of a gas or of a flame. The measurement of flame temperatures will be discussed later (Chap. XIII and Exp. 17). The present discussion is limited to cases in which the bodies to which temperature numbers are to be assigned are free of all electrical and chemical changes and in which the introduction of the temperature measuring device does not give rise to such changes.

Having identified heat with the internal molecular energy of a body, it is natural to try to devise a measure of heat in terms of, say, average molecular kinetic energy. But attempts to assign dimensions<sup>1</sup> to temperature on the usual mass-length-time system of dimensions have not been successful. Hence it may be expedient to define temperature as itself one of the (arbitrary) fundamental dimensions. Another viewpoint is possible. According to it, temperature is dimensionless, since the operation of measuring temperature always reduces to a dimensionless ratio of lengths, pressures, etc. Either viewpoint implies that when the statement "heat is energy" is written as an equation, it includes a dimensional constant.

### Temperature scales

Temperature can be measured only by indirect methods, generally by transferring heat to an instrument designed to respond to the energy so transferred. Any gross physical property which changes with temperature in a reproducible manner can, at least in principle, be used to measure tempera-

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<sup>1</sup> A. G. Worthing, *Am. J. Physics*, **8**, 28 (1940).

R. C. Tolman, *Phys. Rev.*, **9**, 237 (1917).

P. W. Bridgman, *The Logic of Modern Physics*, New York, 1928, pp. 117-124.

L. Balamuth, H. C. Wolfe and M. W. Zemansky, *Am. J. Physics*, **9**, 199 (1941).

ture. Changes in the properties listed in Table I have been found most useful for practical temperature measurement.

The process of assigning numbers to temperatures is partly analogous to the process of marking divisions on a tape measure. The zero is arbitrary. The scale is continuous, that is, an infinity of thermal states can be represented between the arbitrarily-chosen fixed points.

To assign numbers to temperatures we select (i) some suitable substance, then (ii) some property of this selected thermometric substance, and finally (iii) some function relating the temperature to this property. The temperature scale so defined will be only one of a large number of possible ones. It will depend in general on all three selections—the thermometric substance, the property and the function. Any such thermometric device ceases to be useful for defining a scale if its thermometric property ceases to change as heat is abstracted from it or if it undergoes such changes owing to use that, when it returns to its original thermal state after

TABLE I

Thermometric substance	Thermometric property	Symbol
Gas or vapor at constant volume.....	Pressure	<i>P</i>
Mercury in glass capillary.....	Volume	<i>V</i>
Platinum wire.....	Electrical resistance	<i>R</i>
Thermocouple.....	Thermal e.m.f.	<i>E</i>
Dilatometer or bimetal strip .....	Length	<i>L</i>

such use, it gives a reading differing significantly from the original one.

Suppose we select as basic fixed points the melting point of ice and the boiling point of water, each at a pressure of one standard atmosphere, and assign to them the numbers 0 and 100, respectively. We can define a scale by making equal increments on the scale correspond to equal increases in length of a tungsten rod. Thus 50° would be the tempera-

ture at which the length of the rod is halfway between its length at  $0^\circ$  and its length at  $100^\circ$ , or in general

$$t = 0^\circ + \frac{L_t - L_0}{(L_{100} - L_0)/100}$$

Are the degree intervals on this scale equal? Experience shows that the length of a rod of copper will be halfway between its length at  $0^\circ$  and its length at  $100^\circ$  at a temperature which on our tungsten rod expansion centigrade scale is  $54^\circ$ . If we divide up the interval in proportion to the change in electrical resistance, the resistance scale based on copper will agree with the expansion scale based on tungsten to within a very small fraction of a degree. The resistance scale based on tungsten agrees with none of the other three. Which property divides the scale equally? Which material? Aside from this, the linear function chosen, even though the simplest choice, is entirely arbitrary.

This illustrates a fundamental property of temperature which is often lost sight of, namely that temperature is an *intensive* and not an extensive quantity. There can be no unit temperature interval, which can be successively applied to measure any other temperature interval as can be done in the measurement of such a quantity as length. The size of a degree on one part of a scale, no matter how defined, can bear no relation to the size of a degree on any other part of the scale.

The various temperature scales that have been and still are in use differ in the thermometric substance employed, the thermometric property utilized, or in the function selected to represent the relation between the property and the temperature. Scales which differ in either of the first two features are fundamentally different. The difference between two scales, which differ only in the function chosen, is only superficial, because conversion from one scale to the other is merely a matter of the calculation and can be made with mathematical precision. Changing the numbers assigned

to the fixed points makes no real change in the character of the scale and is perhaps the simplest way that the interpolation function can be changed. Thus we have the centigrade, Fahrenheit and Réaumur scales, on which the fundamental interval from the ice point to the steam point is divided, respectively, into 100, 180, and 80 intervals of  $1^\circ$  each. In the original forms, the ice point was designated, respectively,  $0^\circ\text{C.}$ ,  $32^\circ\text{F.}$  and  $0^\circ\text{R.}$ , and conversion from one scale to the other is made as follows:

$$n^\circ\text{C.} = (0.8n)^\circ\text{R.} = (1.8n - 32)^\circ\text{F.}$$

It is sometimes convenient to increase all the numbers for temperatures on these scales by a suitable, constant amount, in order that the lower limit of temperature ("absolute zero") shall be designated as  $0^\circ$ . The amount by which a scale should be increased to accomplish this result depends upon the thermometric property and cannot be known exactly, since it must be experimentally determined. However, since the amount by which a scale has been shifted in any given case is known, this shift can be taken care of with mathematical precision.

In contrast, two scales which employ either different thermometric substances or different thermometric properties differ by an amount which can be determined only by experiment. If the same basic fixed points are employed the scales will necessarily agree at these points, but not at other points. Two scales, both based on the apparent expansion of mercury in glass, will differ unless the kind of glass used is the same. The scale based on the change in pressure, at constant volume, of a definite mass of nitrogen differs from the scale based on the change in volume of the same gas at constant pressure. The constant-volume nitrogen scale with initial pressure (at the ice point) of 500 mm. Hg differs from the constant-volume nitrogen scale with 1000 mm. initial pressure.

The ideal temperature scale would be one which made use of a property so selected that the scale would not depend

on the thermometric substance. Such a scale would serve throughout the entire temperature range, since no limitations due to failure or breakdown of any substance would be met. The only scales of this kind that have so far been devised will be described in Chap. XII.

### Early air thermometers

The first approximate thermometer or thermoscope was probably invented by Giambattista della Porta (1511–1615), although it is generally attributed to Galileo (1561–1612) who used it about 1597. Air was confined in a bulb connected to a vertical tube in which moved an index of colored alcohol (Fig. 1). The air was practically at the constant pressure of 1 atmosphere.

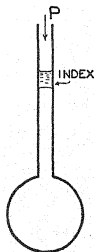


FIG. 1.—Galileo thermoscope.

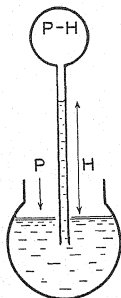


FIG. 2.—Drebbel thermoscope.

variable volume thermometer and also the idea of multiplying a dilatation geometrically. About 1620 Cornelius Drebbel, a Dutch peasant, invented the form of thermometer shown in Fig. 2. In 1702 the physicist-inventor Amontons designed a constant volume air thermometer. He proposed to define temperature ratios in terms of the corresponding pressure ratios;  $T_1/T_2 = p_1/p_2$ . He assigned numerical values to temperatures taking as an arbitrary reference point water boiling under a pressure of 1 atm. Amontons' advanced ideas were long in receiving recognition, but the instrument thus conceived later became the standard gas thermometer.

### Early liquid thermometers

Water thermometers were used at the beginning of the 17th Century. Galileo (1611) constructed an open spirit

thermometer. By 1630 the Academie florentine del Cimento used a sealed type which permitted measurements of higher temperatures and made the readings independent of barometric pressure. When mercury was first substituted for alcohol about 1680 many of the difficulties of liquid thermometry were resolved. Mercury is easier to obtain pure. Its useful range is greater. Because it is opaque and brilliant the position of a mercury column is easy to read. The variable expansion of the envelope and the arbitrary nature of the calibration were the principle difficulties which remained in the application of liquid thermometry.

Joachim d'Alencé wrote one of the earliest treatises<sup>2</sup> in which he mentioned as so-called fixed points for the calibration of thermometers, the temperature at which butter melts, the temperature of a very deep cellar, and the temperature of a mixture of ice and salt.

About 1724 Fahrenheit, a Danzig glass blower, popularized mercury thermometers by constructing them with scales in good agreement among themselves. Previously thermometers usually had been supplied with only two reference marks, or none at all, and hence were useful only for qualitative comparisons. Fahrenheit took for the zero of his thermometer the temperature of a mixture of ammonium chloride and ice, while the normal human blood temperature served as the upper reference point. Réaumur (1730) selected the fixed points suggested by Olaf Römer (1702), the freezing point and boiling point of water, and divided the interval into 80 equal parts. Celsius (1742) divided the same interval into 100 parts, assigning 0 to the boiling point and 100 to the freezing point. A year later Linné and Strömer reversed this designation and established what is today called the Celsius scale. Table II is a comparison of the scales in common use.

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<sup>2</sup> *Traitéz des baromètres, thermomètres et notiomètres*, Amsterdam 1688, translated by E. H. Brown and A. C. Brown, *Bull. Am. Ceram. Soc.*, 13, 335 (1934).

The Fahrenheit thermometer is used today in English-speaking countries. The Réaumur thermometer is used in eastern Europe and is also commonly used in Germany where the Centigrade scale is the legal standard. The Centigrade scale is in general use for scientific work and tends to become more widely adopted.

TABLE II  
COMMON THERMOMETER SCALES

	Fahren- heit	Réaumur	Centigrade (Celsius)	Centi- grade ab- solute or Kelvin	Fahren- heit ab- solute or Rankine
Symbol.....	°F.	°R.	°C.	°K.	°R.'
Temperature in condensing steam.....	212	80	100	373.16	671.69
Temperature in melting ice.	32	0	0	273.16	491.69
Temperature at absolute zero.....	-459.69	-218.53	-273.16	0	0
Number of divisions in the fundamental interval....	180	80	100	100	180
Country of origin.....	Germany	France	Switzerland	England	England

For meteorological purposes thermometers are required to indicate the maximum and minimum temperatures to which they have been exposed during a certain period. Maximum thermometers and minimum thermometers were first prepared by Cavendish (1760). James Six constructed a combined maximum and minimum thermometer in 1782. This type (Fig. 3) is provided with two scales increasing in opposite directions. The maximum and minimum temperatures are indicated by the positions of small iron indexes in the vertical tubes which are moved by a rising column of mercury but which are prevented by friction from moving when the column falls. The indexes are reset with the aid of a small magnet. Modern Six thermometers use beech creosote as the thermal-reacting fluid and mercury as the temperature-indicating fluid.



Beckmann thermometers are used to measure accurately small differences in temperature. The stem is graduated to show a few degrees only, and each degree is subdivided into

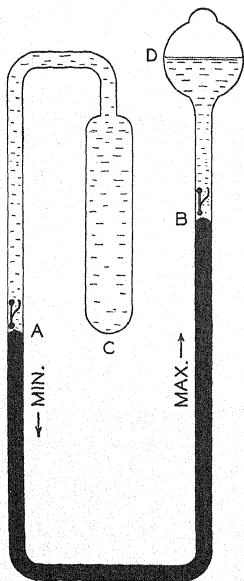


FIG. 3.—Maximum-minimum thermometer.



FIG. 4.—Beckmann thermometer (Central Scientific Co.)

hundredths. The top of the tube is bent over so as to form a chamber into which some of the mercury may be shaken (Fig. 4). Sufficient mercury is left in the bulb to enable the

lower temperature to be read. The higher temperature is then read, and the difference in the readings gives the required difference in temperature. Such thermometers have the advantages of greater sensitivity without the necessity of employing a very long stem.

Since the middle of the last century, technical and scientific demands have required improvements of thermometers to attain higher temperature ranges, greater accuracy and more rapid response.

### Liquid thermometers

Mercury and other thermometric liquids differ in capillary effect and in so many other characteristics that it is customary to make an arbitrary distinction between mercury thermometers and liquid thermometers in discussing thermometry.

### Correction for emergent stem of thermometer

If the mercury thread of a thermometer is not at the same temperature as the bulb, the emergent stem correction may be too large to be neglected. The correction for the emergent stem may be computed from the formula:

$$\text{Stem correction} = Kn(t_b - t_s)$$

$K$  = Factor for relative expansion of mercury in glass, 0.00015 to 0.00016 for centigrade thermometers, 0.000083 to 0.000089 for Fahrenheit thermometers, at ordinary temperatures, depending upon the glass of which the stem is made. For ordinary calorimetric thermometers graduated on the Fahrenheit scale, the value  $K = 0.000085$  may be used.

$n$  = number of degrees emergent from the bath.

$t_b$  = temperature of the bulb.

$t_s$  = mean temperature of the emergent stem.

### Effect of filling gas

Distilling of the thermometer liquid is prevented by the addition of a gas whose pressure elevates the boiling point.

To avoid reaction with the liquid, dry nitrogen or hydrogen is generally used as the filling gas. Air or carbon dioxide is not suitable. By this device, and by using a quartz envelope, the range of a mercury thermometer can be extended from  $360^{\circ}$  to  $600^{\circ}\text{C}$ . The pressure  $p$  of the supernatant gas is not constant for a given thermometer, due to (i) variation of gas pressure with temperature:  $p_t = p_o(1 + \alpha t)$ ; (ii) variation of volume of indicating liquid with temperature:  $p_v = p_o v_o$ ; (iii) irregular dependence of volume on temperature and pressure due to the elasticity of the glass envelope; (iv) compression of the thermometric fluid, often very different at different pressures and temperatures; (v) absorption or reaction of gas with glass at different pressures and temperatures; (vi) diffusion of gas through walls.

If  $\beta$  is the coefficient of compressibility of the liquid,  $\alpha_L$  its cubic expansion coefficient, and  $\alpha_g$  the cubic expansion coefficient for the gas (approximately  $\frac{1}{273}$  per deg. C.), the change in liquid volume due to a change in gas pressure in a rigid envelope is

$$\Delta v_t = \beta p_t v_t = \beta p_o(1 + \alpha_g t) v_o(1 + \alpha_L t)$$

The net rate of change of volume with temperature is

$$\frac{dv}{dt} = v_o(1 + \alpha_L t) - \Delta v_t.$$

Calibration over the entire scale, not merely at a few fixed points, is necessary due to variations in capillary diameter and variations in the expansion coefficient of an organic liquid.

### Indicating liquids

Liquids commonly used in thermometry are listed in Table III. Freezing and boiling points depend on the impurities present. Many thermometers contain mixtures of these liquids or have color added.

For low temperatures organic substances ordinarily not liquid at room temperature are used. For high temperatures gallium-in-quartz thermometers are serviceable to 1000°C.

TABLE III  
LIQUIDS USED FOR THERMOMETRY<sup>3</sup>

Name	Formula	Expansion coefficient $\alpha$ at 18°C.	Freezing point °C.	Boiling point °C.
1. Methyl alcohol...	CH <sub>3</sub> OH	0.00122	- 93.9 to - 97.8	64.2 to 66.0
2. Ethyl alcohol....	C <sub>2</sub> H <sub>5</sub> OH	.0011	-111.8 -117.3	77.7 78.4
3. Alcohol.....	C <sub>2</sub> H <sub>5</sub> OH 96 %	.....	-117	78.17
4. Propyl alcohol...	C <sub>3</sub> H <sub>7</sub> OH	.....	-127.0	97.2 97.4
5. Butyl alcohol....	C <sub>4</sub> H <sub>9</sub> OH	.....	- 79.9	34.5
6. Amyl alcohol....	C <sub>5</sub> H <sub>11</sub> OH	.00093	.....	137.0 137.8
7. Glycol.....	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	.....	- 11.5 - 15.6	197.0 197.5
8. Petroleum.....	.....	.00092	.....	.....
9. Petroleum ether..	.....	.....	.....	.....
10. Pentane.....	C <sub>5</sub> H <sub>12</sub>	.....	-130.8 -147.5	36.0 36.5
11. Pentane (tech.)..	Mixture	.....	below -200	.....
12. Toluol.....	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	.00109	- 92.4 -102.0	109.2 110.6
13. o-xylene.....	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	.....	- 27.1 - 45.0	142.0 145.0
14. m-xylene.....	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	.00101	- 53.0 - 54.8	139.0
15. Acetone.....	CO(CH <sub>3</sub> ) <sub>2</sub>	.00131	- 93.9 - 94.9	56.3
16. Aniline.....	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	.00085	- 6.0 - 8.0	183.8
17. Creosote (beech wood).....	Mixture	.....	- 25 - 45	210
18. Carbon disulphide	CS <sub>2</sub>	.00121	-113.0	46.0
19. Mercury.....	Hg	.000181	- 38.87	356.7

In time the thermometer liquid may suffer polymerization resulting in a contraction and a lowering of the zero point. Such change is often apparent through discoloring of a formerly clear liquid. The average depression of the freezing point of 8 thermometers tested by Grundmann after 4½ years was 0.73°C. Such change is hastened by exposure to light, especially ultraviolet radiation. In fact in the same tests a change of 0.9°C. was produced in 150 hr. under an ultra-

<sup>3</sup> W. Grundmann, *Glas u. App.*, 17, 59 (1936).

violet lamp. Gradual contraction of the thermometer glass with time partially compensates for the depression of the zero due to polymerization of the thermometer liquid. Exposure to suitable light and heat treatment before calibration hastens the establishment of an equilibrium and permits thermometer calibrations which are more permanent, as has been shown experimentally. The chief disadvantage of liquid thermometers as compared with mercury thermometers is that in time they develop a relatively larger depression of the zero.

### Thermometer lag

A thermometer is in equilibrium with the material whose temperature is to be measured only when an equilibrium is established for both heat conduction and radiation. Measurement of atmospheric temperature is influenced by the color and surface of the thermometer. A free-hanging thermometer attains an equilibrium with its entire surroundings including the varying radiation. Hence for measuring atmospheric temperature a thermometer shielded from radiation is used. The air temperature is defined as proportional to the kinetic energy of its molecules only and not that of a volume of radiation.

The thermal conductivity of the glass envelope of a radiation-shielded thermometer depends on the form, surface, weight, material, thickness and conductivity of the envelope and on the convection around the thermometer. The rate of heat exchange between a thermometer and its surrounding increases with increase in its surface  $A$ , with decrease in its total heat capacity  $MC$ , and with increase in its outer conductivity  $K$ .

The lag of the temperature  $T'$  indicated by a thermometer in material of constant temperature  $T$ , assuming the inner conductivity very large, is given by

$$T - T' = \frac{V\rho C}{KA} \frac{dT'}{dt} = \alpha \frac{dT'}{dt} \quad (1)$$

Here  $dT'/dt$  is the change in temperature per minute and  $\alpha$  is defined as the lag coefficient of the thermometer. In integrated form, Eq. 1 becomes

$$T - T' = (T - T_i)e^{-\frac{t}{\alpha}} \quad (2)$$

$T_i$  is the initial temperature of the thermometer. Nernst called  $T = T'$  (for  $t = \infty$ ) the convergence temperature. The ideal of a thermometer without lag is approached by very small thermocouples and resistance thermometers of small heat capacity.

Table IV shows that for common thermometer fluids the product  $\rho C$  is practically constant. It follows from Eq. 1 that mercury and liquid thermometers of the same form have nearly equal lag.

TABLE IV  
THERMAL CAPACITY OF THERMOMETER FLUIDS<sup>3</sup>

Material	Thermal capacity C cal./gm. °C.	Density $\rho$ gm./cm. <sup>3</sup>	$\rho C$
Glass.....	0.19	2.5	0.47
Mercury.....	.033	13.6	.45
Ethyl alcohol.....	.58	0.79	.46
Amyl alcohol.....	.50	.81	.41
Toluene.....	.41	.89	.37

The integral of Eq. 1 is

$$\log (T' - T) = \log a' - \frac{t}{\alpha} \log e = a - \frac{0.43}{\alpha} t \quad (3)$$

The use of this equation in the experimental calculation of  $\alpha$  is illustrated by Table V, which contains data for a creosote-filled thermometer whose bulb has a diameter of 15.1 mm. and length 24.5 mm.

<sup>3</sup> W. Grundmann, *Glas u. App.*, 17, 59 (1936).

It is probably better to use a liquid whose lag coefficient  $\alpha$  is rather large but constant over the region of measurement in preference to a liquid having a small but variable lag coefficient. Alteration of  $\alpha$  with time, due to viscosity changes, generally can be avoided by appropriate pre-treatment of the liquid, i.e., by thermal massage.

TABLE V  
EXPERIMENTAL EVALUATION OF  $\alpha$

$T$ °C.	$T'$ °C.	$t$ min.	$\log (T' - T) = a - \frac{0.43}{\alpha} t$
-5.0	35.0	0	$1.60 = a$
-5.0	30.0	0.08	$1.54 = a - \frac{0.03}{\alpha}$
-5.0	25.0	.18	$1.48 = a - \frac{0.08}{\alpha}$
-5.0	20.0	.30	$1.40 = a - \frac{0.13}{\alpha}$
.	.	.	.
.	.	.	.
-5.0	-4.0	2.21	$0.00 = a - \frac{0.95}{\alpha}$
			$\alpha = 0.62$

### Influence of coloring material

Most thermometric liquids (Table III) are colorless. When a dye is added to increase the visibility of the meniscus it may introduce new sources of error. Contamination of the capillary and decrease in the bulb size result in an elevation of the zero. Chemical reaction with the glass capillary or the formation of a solid solution increases adhesion in the capillary and hinders smooth recession of the liquid column. Hence precision thermometers use colorless or lightly-colored liquids. Coloring matter may serve as a catalyst for physical or chemical changes, mostly those influenced by light absorp-

tion. This is especially apparent in thermometers whose liquid contains acetone.

One type of thermometer avoids these errors by coloring a strip of glass rather than the liquid. Figure 5 shows a section of such a tube.<sup>4</sup> Behind the capillary bore is a red or blue strip backed by a broader one of white or yellow. An observer at *A* sees red only when there is liquid in the bore. Rays 1, 2 and 3 are totally reflected from that part of the bore which is empty.

#### Influence of alteration of thermometer glass

The physical properties of different types of glass depend chiefly upon their composition and heat history. Glass is a super-cooled liquid. Alterations in the solution are dependent upon temperature and previous thermal and elastic working of the glass. By heating to 450–500°C. and cooling slowly (or by rapid heating and cooling for many hours) one tries to establish an equilibrium that will prevent further shrinking of the glass. However, a completely stable equilibrium independent of temperature is scarcely possible. In time the glass attains equilibrium at each temperature, but for large changes in temperature it is more or less distorted. In the reversible changes to which the glass is subjected the volume attains a constant value only gradually after a sudden change in temperature. There exists also an irreversible change associated with the gradual change of the glass from an amorphous to a crystalline form, resulting in a decrease in volume and an elevation of the thermometer zero. A thermometer of unannealed soft glass may experience a calibration change of 20°C. with prolonged heating, while

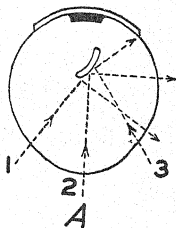


FIG. 5.—Colored-strip thermometer.

<sup>4</sup> *Chem. Fab.* 12, 403 (1939), from Kuhlens and Reinhardt, *Pharm. Ind.*, 6, 310 (1939).



the change may be  $10^{\circ}\text{C}$ . for one of unannealed hard glass. A thermometer of hard sodium-free glass which has been annealed may suffer a zero elevation of about  $0.03^{\circ}\text{C}$ . the first year and  $0.01\text{--}0.02^{\circ}\text{C}$ . the second year.

### Accuracy of liquid thermometry

The principle sources of error in the installation and testing of thermometers are:

Insufficient immersion.

Lack of temperature equilibrium in the test bath.

Sudden chilling and undercooling of the thermometer.

Sticking of fluid particles in the capillary.

Condensation in that part of the capillary not filled with liquid.

Non-uniformity of the capillary bore.

For work of high precision it is necessary to determine whether the thermometer is sensitive to position. The density of mercury may make the thermometer readings dependent on the angle the thermometer tube makes with the vertical.

Table VI lists the maximum tolerances in thermometer scale errors allowed by the specifications of the National Bureau of Standards, the American Society for Testing Materials and the Physikalisch-Technische Reichsanstalt. The NBS and PTR tolerances are for uncorrected scale readings. If they are exceeded by a thermometer under test, no certificate is issued. A thermometer which meets the specifications is calibrated at many temperatures and a correction curve is drawn for its entire range. It is assumed that corrections from this calibration will be applied consistently to all readings taken with the thermometer. If this is done, the results obtained with the thermometer are, of course, more accurate than the tolerances listed.

The ASTM specifications represent a different viewpoint. They require thermometer readings to have a certain accuracy, without the application of scale corrections. In general,

TABLE VI  
TOLERANCES IN THERMOMETER SCALE READINGS<sup>5</sup>

Temperature range	Graduation intervals	Scale error tolerance		
		NBS	ASTM	PTR
-190 to -80	.05, .1, or .2	...	.....	1.0
	.5 or 1	...	.....	3.0
- 80     -20	.01 or .02	...	.....	.05
	.05, .1, or .2	...	.....	.5
	.5 or 1	...	.....	1.0
- 35         0	.5 or 1	.5	.1 to .2	
	.2	.4	.02 .5	
- 20       100	.05, .1, or .2	...	.....	.25
	.5 or 1	...	.....	.5
	Greater than 1	...	.....	1.0
Graduated not above 150:				
0       150	.5 or 1	.5	.1 .2	
	.2	.4	.02 .05	
0       100	.1	.3	.01 .03	
Graduated not above 300:				
0       100	.5 or 1	.5	.1 .2	
	.2	.4	.02 .05	
100    300	.5 or 1	1.0	.2 .3	
0       100	.2	.4	.02 .05	
100    200	.2	.5	.05 .1	
100    200	.05, .1 or .2	...	.....	.5
	.5 or 1	...	.....	1.0
	Greater than 1	...	.....	2.0
200       300	.5 or 1	...	.....	2.0
	Greater than 1	...	.....	3.0
300       400	.5 or 1	...	.....	3.0
	Greater than 1	...	.....	5.0
Graduated above 300:				
0       300	.2	.2	.2 .5	
	.5 or 1	.4	.5 1.0	
300    500	.2	.4	.2 .5	
0       300	.5 or 1	.2	.1 .5	
400       700	.5 or 1	...	.....	5.0
	Greater than 1	...	.....	9.0

<sup>5</sup> E. F. Mueller and R. M. Wilhelm, *Proc. Am. Soc. Testing Materials*, **38**, 1 (1938), 493.

W. Grundmann, *Glas u. App.*, **18**, 65 (1937).

the ASTM specifications call for a better thermometer to attain a somewhat less reliable result than could be obtained by applying corrections.

### Liquid-in-metal thermometers

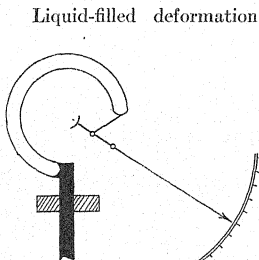


FIG. 6.—Bourdon-tube thermometer.

Liquid-filled deformation thermometers are generally of the Bourdon tube type. A flat metal tube, usually brass, of more or less ring shape is filled with liquid at a temperature below the lowest temperature at which it will be used. With one end clamped (Fig. 6), the motion  $dS$  of the free end is related to the temperature  $t$  by

$$dS \div LR\alpha'dt \quad (4)$$

where

$$R = \left( 1 + \frac{\sin^2 \phi}{\phi^2} - \frac{2 \sin \phi \cos \phi}{\phi} \right)^{1/2} \quad (5)$$

and  $L$  = effective length of the Bourdon tube;  $\alpha'$  = difference of volume coefficients of expansion of liquid and tube, respectively;  $\theta$  = central angle of arc; and  $\phi = \theta/2$ .

For amyl alcohol in a brass tube  $\alpha' = 8.73 \times 10^{-4}$  at room temperature. The value of  $\alpha'$  increases with temperature. Alterations occur with time in both the liquid and in the tube.

### Bimetal thermometers

A bimetal thermometer consists of strips of two metals having different expansion coefficients, riveted, soldered or welded together. With one end clamped, the deflection  $dS$  of the free end is related to the temperature by

$$\frac{dS}{dt} = \frac{4L^2R\alpha'}{5\delta\theta} \quad (6)$$

where  $L$  = effective length of the bimetal;  $\alpha'$  = difference between the two linear expansion coefficients;  $\delta = \frac{d_1 + d_2}{2}$ , the average of the two thicknesses.  $R$  and  $\theta$  have the same significance as in Eq. 5. In contrast with a Bourdon tube,  $dS/dt$  for a bimetal is greatest for a straight strip ( $\theta = 0$ ).

When the bimetal is made in a spiral form,  $dS/dt$  is greater than for a simple bimetal ring of the same heat capacity.

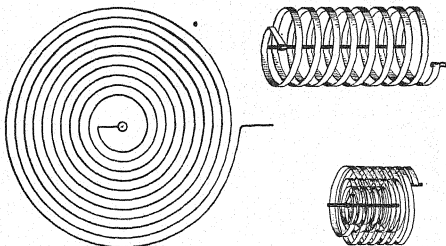


FIG. 7.—Relative size of three types of bimetal elements having the same torque and deflection. (*Weston Electrical Instrument Corp.*)

But the force  $F$  for a spiral is much decreased compared with that of a single ring having the same mass or the same value of  $dS/dt$ .

$$F \div \frac{MI}{L^3} \div \frac{M\delta^3 B}{L^3}$$

where  $L$  = effective length;  $B$  = width;  $\delta$  = arithmetic mean of both thicknesses;  $M$  = elastic modulus;  $I$  = moment of inertia of the cross section.

Figure 7 illustrates the relative size of three types of bimetal elements having the same torque and deflection. In the multiple helix the several coils are additive in rotational deflection, but the axial displacement is mutually counterbalanced.

Thermal lag depends upon mass and specific heat. For similar precision, a bimetal element can be made more compact than a Bourdon tube, and hence has a smaller lag. A bimetal element will withstand excessive high temperatures with less subsequent change in its scale than will a Bourdon tube, but if subjected to excessive low temperatures changes in the bonding material may result in irregular readings. A new bimetal thermometer shows considerable decrease in  $dS/dt$  over a period of time. This may be minimized by thermal massage before the thermometer is calibrated. Bimetal thermometers for industrial use have accuracies comparable to those of industrial mercury thermometers.

### Gas thermometers

A gas, confined in a volume which is strictly constant and at uniform temperature throughout, exerts a pressure which is a function of the temperature. This pressure may be used to define a scale of temperature according to the equation

$$p = cT_g \quad (V \text{ constant}) \quad (7)$$

where the subscript  $g$  indicates that the scale depends on the kind of gas and on its density, and does not necessarily agree with the thermodynamic scale (Chap. XII). The constant  $c$  is fixed by the condition that  $T_g$  increase by  $100^\circ$  in passing from the ice point to the steam point. The constant  $c$  is equal to the product of the pressure coefficient of the gas  $\beta$  and the pressure of the gas at the ice point ( $c = \beta p_o$ ).

To realize a definite gas scale of temperature it is necessary to take into account the fact that no actual gas thermometer quite fulfills the conditions expressed above. The volume always changes somewhat with changes in temperature and pressure. Also there is always some gas in the capillary and other pressure-transmitting volumes  $V_i$  that is not in general at the same temperature as the gas in the

thermometer bulb. These facts make it necessary to work with the product  $pV$  in place of the single variable  $p$  of Eq. 7. Referring to unit mass of gas, consider the equation

$$pv = aT_g \quad (8)$$

For any given value of  $v$  this may be made identical with Eq. 7 by making  $a/v = c$ , so that there are exactly  $100^\circ$  between the ice and steam points. If  $a$  is kept fixed while  $v$  is allowed to vary, the temperature  $T_g$  corresponding to a given thermal state is no longer uniquely defined by Eq. 7, but may range over a narrow band of values whose width is proportional to the deviation of the gas from Boyle's law. Evidently the ice-to-steam interval will in general be  $100^\circ$  only for one particular gas density. Let  $a$  be so chosen that the particular density for which this occurs is the same as the density of the gas in the bulb of a constant-volume gas thermometer. Then, if the total volume of the gas thermometer is  $V$  and the mass of gas contained is  $m$ ,

$$pV = maT_g \quad (9)$$

if the entire thermometer is at uniform temperature. If it is not at uniform temperature, imagine it subdivided into smaller volumes, each of which may be considered to be uniform in temperature. For the gas in each we may write

$$pV_i = m_i a T_{gi} \quad (10)$$

and summing over all the volumes

$$p \sum_i \frac{V_i}{T_{gi}} = a \sum_i m_i = A = \text{constant}$$

Separating and dropping subscripts on the important term which refers to the gas-thermometer bulb,

$$p \left\{ \frac{V}{T_g} + \sum_i' \frac{V_i}{T_{gi}} \right\} = A \quad (11)$$

the prime indicating that one of the terms has been taken outside the summation. Variations in the bulb volume may be taken into account by writing

$$\begin{aligned} V &= V_o(1 + \alpha T + \beta T^2 + \dots + \gamma p + \epsilon p^2 + \dots) \\ &= V_o[1 + f(T, p)], \end{aligned}$$

the constants being determined by preliminary investigations. Substituting this expression in Eq. 11 and multiplying by  $T_g/V_o$ , we obtain

$$p \left\{ 1 + f(T, p) + \frac{T_g}{V_o} \sum_i' \frac{V_i}{T_{gi}} \right\} = \frac{A}{V_o} T_g$$

and putting  $V_o/A = C$ ,

$$T_g = C \left\{ 1 + f(T, p) + \frac{T_g}{V_o} \sum_i' \frac{V_i}{T_{gi}} \right\} p \quad (12)$$

From this equation,  $T_g$  may readily be found by successive approximations since only the first term in the braces is large. In the calculations it is generally permissible to use  $T_g$  for  $T$  in finding the change in bulb volume with temperature. The change in bulb volume with pressure is in many cases negligible. The pressure-transmitting volumes,  $V_i$ , must be found by actual measurement, but their change with temperature and pressure may ordinarily be neglected. The temperatures  $T_{gi}$  which should be assigned to the transmitting volumes are really defined by Eq. 10. However, they are ordinarily measured with thermometers or thermocouples calibrated to give temperatures in approximate agreement with the thermodynamic scale. With data on the deviation of the gas from Boyle's law one may calculate how the value of  $T_{gi}$  corresponding to a given thermal state will vary as the gas density is changed. For most gases this variation is small, seldom more than a few hundredths of a degree throughout the range of densities likely to occur in a gas-thermometer system. Hence, since the  $T_{gi}$ 's occur

only in small correction terms, it is generally permissible to replace them directly with thermometer and thermocouple indications of  $T$ .

Experimental determination of the constant  $C$  requires in principle that  $p$  be measured at both the ice and steam points. In many instances it is better to determine  $C$  from measurements made at a single point, employing the results of earlier investigations to insure the preservation of the 100° ice-to-steam interval. It is worth-while to emphasize that when  $C$  is determined without measuring the ice-to-steam interval, the gas-scale temperature  $T_g$ , rather than the thermodynamic temperature,  $T$ , of the calibration point must be inserted in Eq. 12.

To obtain centigrade gas-scale temperatures from temperatures on the corresponding absolute gas scale, the temperature of the ice point on the latter scale must be subtracted,

$$t_g = T_g - T_{g0}$$

### Reduction of gas thermometer temperatures to the thermodynamic scale

The most common method of reducing gas-scale temperatures to the thermodynamic scale is based on the assumption that when a gas is used at lower and lower densities, the corresponding gas scale approaches the thermodynamic. Data for helium which permit this extrapolation to zero density have been obtained both at the Reichsanstalt and at Leiden and tables of corrections based on these data have been published. These corrections are for a centigrade gas scale and are consequently zero at the ice and steam points. To facilitate a comparison of the results of the two laboratories, the corrections which they would obtain for the same gas have been computed<sup>6</sup> and are plotted in Fig. 8. The heavy line on this graph is a weighted mean of the two sets of values.

<sup>6</sup> H. J. Hoge and F. G. Brickwedde, *J. Research Nat. Bur. Standards*, **22**, 351 (1939).



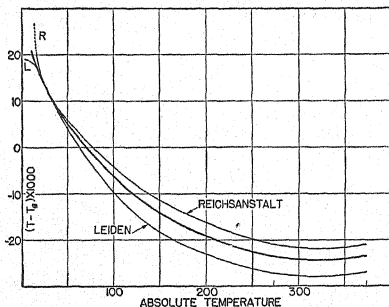


FIG. 8.—Corrections to gas thermometer scales for reducing to the thermodynamic scale. (H. J. Hoge and F. G. Brickwedde, *J. Research Nat. Bur. Standards*, 22, 351, 1939.)

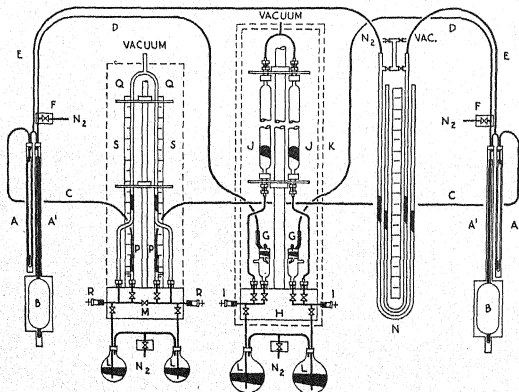


FIG. 9.—Precision (double) gas thermometer. (J. A. Beattie, *publication pending*)

### Types of gas thermometers

Measurements made with a constant volume gas thermometer of simple type may be corrected for the effect of the change in volume of the container and for the effect of the pressure-transmitting volume by calculations of the type outlined in Exp. 1. In measurements of high accuracy this is usually accomplished by competition rather than by calculation. An auxilliary tube similar to the tube connecting the thermometer bulb to its manometer is so arranged that the contribution of  $\sum_i' \frac{V_i}{T_{gi}}$  [Eq. 11] annuls the corresponding term referring to the pressure transmitting volume of the thermometer proper.

A modern precision gas thermometer is illustrated in Fig. 9. This is a double thermometer. *H* is the main manometer which is thermostated. *M* is an auxiliary manometer for the auxiliary thermometer *A* which determines the mean reciprocal temperature of the capillary *A'*. *N* is the manometer for determining the pressure in the steel cases surrounding the thermometer bulb *B*.

### Summary

Temperatures are indicated in terms of easily-measured physical properties which change with temperature in a reproducible manner. Of these, expansion thermometry is concerned chiefly with the expansion of a gas, vapor, liquid or metal. The definition of a practical temperature scale involves the choice of easily-reproducible fixed points, the division of the fundamental interval into a convenient number of degrees and the choice of an arbitrary zero. Accuracy in liquid thermometry demands: (1) sufficient immersion, (2) temperature equilibrium, (3) avoidance of depression or elevation of the thermometer zero by overheating or undercooling of the thermometer, and (4) care in having the capillary of uniform bore—in short, using

the thermometer under the conditions for which it was calibrated.

### References (General works on temperature measurement)

- American Institute of Physics, *Temperature—Its Measurement and Control in Science and Industry*. New York: Reinhold, 1941.
- Burgess, G. K. and Le Chatelier, H. *The Measurement of High Temperatures*. New York: John Wiley, 1912.
- Cork, J. M. *Heat*. New York: John Wiley, 1937.
- Edser, E. *Heat for Advanced Students* (rev.), New York: Macmillan, 1936.
- Foote, P. D., Fairchild, C. O. and Harrison, T. R. *Pyrometric Practice*, Washington: Bur. Standards Tech. Paper No. 170, 1921.
- The Physical Society Reports on Progress in Physics, London, Yearly volumes: I, 1935 . . . sections on Heat.
- Preston, T. *The Theory of Heat* (rev.), London: Macmillan, 1929.
- Ribaud, G. *Mesure des températures*, Paris: A. Colin, 1936.
- Saha, M. N. and Srivastava, B. N. *A Treatise on Heat*, Allahabad: Indian Press, 1935.
- Veron, M. *Cours de chauffage industriel*, Paris: Laboratoire du Conservatoire des Arts et Métiers, 1935.
- , "Evolution historique des idées sur la repérage des températures," *Chaleur et Ind.*, 18, 395–400; 473–476 (1937).
- Wood, W. P. and Cork, J. M. *Pyrometry*, New York: McGraw-Hill, 1927.
- The Journal of Applied Physics*, 11, No. 6, 1940 [Special issue on measurement and control of temperature].

### Problems

1. At what temperature does the Fahrenheit thermometer read (i) the same, (ii) half, (iii) twice as much as the centigrade thermometer?
2. Let  $X_0$  and  $X_{100}$  be the values of a thermometric property at the ice and steam points, and  $X_t$  its value at the temperature  $t$ . Then the temperature may be determined on the centigrade scale from

$$t = \frac{X_t - X_0}{X_{100} - X_0} 100.$$
 Write the corresponding equation for the Fahrenheit scale.

3. State several reasons why a mercury-in-glass thermometer may not be a reliable temperature standard.

4. A centigrade thermometer placed in a hypsometer containing boiling water reads  $98.0^{\circ}\text{C}$ . The barometer reads 720.2 mm. of mercury. Find the boiling point error of the thermometer.
5. A bridge made of steel (coefficient of expansion  $= 10.5 \times 10^{-6}$ ) is 300 ft. long. If the temperature changes from  $-10^{\circ}\text{C}$ . to  $35^{\circ}\text{C}$ . find the alteration in the length of the bridge.
6. Does the value of the coefficient of expansion depend (i) on the units of length, or (ii) the temperature scale? Explain.
7. A compensated pendulum consists of a thin metal tube of length  $l$  filled with a liquid to a height  $h$ . If the mass of the tube is negligible compared with that of the liquid, show that  $h \doteq 2l\alpha/(\beta - 2\alpha)$ , where  $\alpha$  = coefficient of linear expansion of the tube and  $\beta$  = coefficient of volume expansion of the liquid.
8. Find the change in density of iron when heated from  $0^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ . (coefficient of expansion  $= 3.550 \times 10^{-5}$  per deg. C.)
9. A pyrex flask is calibrated to hold 1 liter at  $0^{\circ}\text{C}$ . How much will it hold at  $100^{\circ}\text{C}$ .? (Coefficient of linear expansion  $= 3.6 \times 10^{-6}$  per deg. C.)
10. Show that the coefficient of superficial expansion of a solid is twice its coefficient of linear expansion.
11. A tire is filled with air at  $60^{\circ}\text{F}$ . to a gauge pressure of 30 lb./in.<sup>2</sup> Find the pressure if the temperature of the tire increases to  $120^{\circ}\text{F}$ ., assuming negligible volume change.
12. From  $L_t = L_0(1 + \alpha t)$ , where  $\alpha$  is the coefficient of linear expansion, derive an expression for the volume expansion.
13. Show that the volume coefficient is approximately three times the coefficient of linear expansion. Interpret the approximation geometrically.

## CHAPTER II

# Heat Transfer

### Introduction

"The science of heating is one of the oldest, most important and least progressive. This may be explained by the dual characteristics of apparent simplicity and real complexity of the production, transmission and transformation of heat."<sup>1</sup> It is the purpose of this chapter to examine the subject of heat transfer under the time-honored headings of conduction,

convection and radiation: and to reach some conclusions of practical value in the design of heat apparatus.

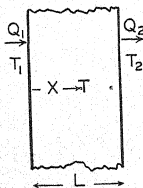


FIG. 10.—Conduction through plane-parallel plate.

### Conduction

#### Thin parallel plate

As a simple example of heat conduction, consider a thin slab of material with parallel faces, one at temperature  $T_1$  the other at  $T_2$  (Fig. 10). Intuition suggests, and experiment shows, that when the temperature at every point has become steady, the amount of heat  $Q$  transferred across the slab in time  $t$  is directly proportional to the temperature difference  $(T_1 - T_2)$ , the area  $A$  of the surface, the time  $t$ , and inversely proportional to the thickness  $l$ , and depends upon the material,

$$Q = \frac{kAt(T_1 - T_2)}{l} \quad (1)$$

<sup>1</sup> M. Veron, *Chaleur et Ind.*, 13, 598 (1932).

While Eq. 1 is strictly valid only for a slab of elementary thickness  $dl$ , it is an adequate approximation in many practical problems.

The coefficient  $k$  is characteristic of the material and is called its thermal conductivity. The units in which conductivity is expressed in the c.g.s. system are: calories per second per square centimeter of area for a temperature gradient of  $1^{\circ}\text{C. per centimeter}$  ( $\text{cal. cm.}^{-1} \text{ sec.}^{-1} \text{ deg.}^{-1} \text{ C.}$ ).

By analogy with electrical resistance, the quantity  $l/k = n$  may be called the thermal resistance of a unit cube. Thermal resistances of conductors in "series" and "parallel" may be calculated from formulas analogous to those used for electrical resistances.

Apparatus for measuring the thermal conductivity of poor and good conductors, respectively, is discussed in Exps. 7 and 8. Another simple method employing unidirectional flow which is capable of high accuracy is illustrated in Fig. 11. Heat is supplied electrically in a central heating plate  $H$ . Slabs  $S$  of the test specimen are placed symmetrically on each side of the heater. Outside these layers are plates cooled by flowing water.  $G$  is a "guard ring" heater to which the power supplied per unit area can be independently controlled and measured. The heater  $G$  takes care of losses of heat from the edges of the specimen  $S$  so that for the area equivalent to that of  $H$  the equitemperature surfaces are sensibly

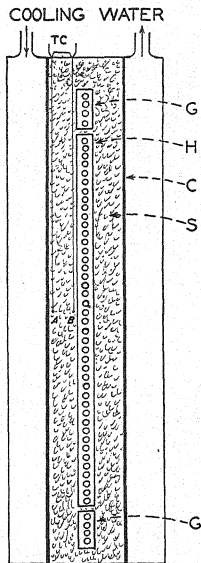


FIG. 11.—Conductivity by parallel plate method.

plane. Differential thermocouples  $ab$  serve to measure the fall in temperature  $(T_1 - T_2)$  across a measured distance  $l$  in the material  $S$ . The conductivity is calculated from

$$K = \frac{EI}{JA(T_1 - T_2)} \quad (2)$$

In this expression  $EI$  is the electrical power in joules per second.  $J$  is the mechanical equivalent of heat, and  $A$  denotes the common area of heater  $H$  and specimen.

### Three-dimensional flow

Fourier's detailed study of problems of heat flow was a notable contribution to physics and mathematics. The methods of analysis and the solutions he developed retain their importance in the study of heat, and, with merely a change in nomenclature, they have been adapted to fit analogous problems in electricity and magnetism.

Let us consider the problem of deriving a differential equation which will describe the conduction of heat in three dimensions inside an isotropic body. Choosing rectangular coordinates, consider a small rectangular parallelepiped (Fig. 12) with its edges parallel to the

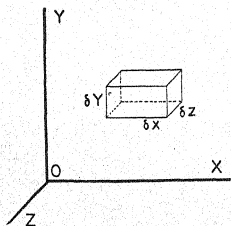


FIG. 12.—Conduction in three dimensions.

coordinate axes. Denote the temperature at the center of the element by  $T$ . The temperature at the left face is then  $T - \frac{1}{2} \frac{\partial T}{\partial x} \delta x$ , that of the right face is  $T + \frac{1}{2} \frac{\partial T}{\partial x} \delta x$ . The heat entering the element through the left face per second in the positive direction of the  $x$ -axis is

$$-k \frac{\partial}{\partial x} \left( T - \frac{1}{2} \frac{\partial T}{\partial x} \delta x \right) \delta y \delta z \quad (3)$$

The heat leaving the element through the opposite face is

$$-k \frac{\partial}{\partial x} \left( T + \frac{1}{2} \frac{\partial T}{\partial x} \delta x \right) \delta y \delta z \quad (4)$$

Hence the net gain of heat per second in the volume element due to the  $x$ -component of the flow is the difference of Eq. 3 and Eq. 4, or

$$k \frac{\partial^2 T}{\partial x^2} \delta x \delta y \delta z$$

Adding similar terms for the flux through the remaining two pairs of faces, the net amount of heat accumulated per second in the element is seen to be

$$k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \delta x \delta y \delta z \quad (5)$$

This will produce a rise in temperature of the element equal to  $\partial T / \partial t$  and hence must be equal to  $\rho C \frac{\partial T}{\partial t} \delta x \delta y \delta z$  where  $\rho$  is the density of the material and  $C$  its heat capacity. Therefore

$$k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) = \rho C \frac{\partial T}{\partial t} \quad (6)$$

Introducing the mathematical operator  $\nabla^2$  for the expression  $\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$ , and substituting  $D = k / \rho C$  the general equation for heat conduction may be written

$$D \nabla^2 T = \frac{\partial T}{\partial t} \quad (7)$$

Kelvin gave the name diffusivity to the constant  $D$ . It is apparent that it is an important factor in determining the velocity of a thermal disturbance through the medium.

### Bar, longitudinal flow

In Exp. 8 no account is taken of the heat lost from the surface of the copper bar since it is small compared to the



quantity conducted along the bar. If, however, it is desired to take account of the radiation loss  $Q_3$  (Fig. 13) the equation for conduction may be written

$$kA \frac{\partial^2 T}{\partial x^2} dx = \rho A dx C \frac{\partial T}{\partial t} + E p t dx$$

Here  $E$  is the emissive power of the surface (energy radiated per unit area per second),  $p$  is the perimeter of a cross section,  $\rho$  is the density,  $C$  the specific heat and  $T$  is the excess of the

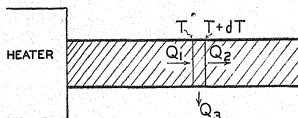


FIG. 13.—Conduction along bar.

temperature of the surface over its surroundings. Putting  $\mu = Ep/\rho AC$  the equation above may be written

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} - \mu T \quad (8)$$

This is the standard Fourier equation for one-dimensional flow of heat. A problem in thermal conduction along a rod consists in finding a solution of this differential equation for given boundary conditions.

### Sphere, radial flow

In the case of the symmetrical flow of heat outward through a spherical conductor (Fig. 14) the quantity of heat flowing per second is

$$-4\pi r^2 \frac{\partial T}{\partial r} k = \text{constant} \quad (9)$$

The variables  $r$  and  $T$  are separable. Integration gives

$$T = \frac{A}{r} - B \quad (10)$$

where  $A$  and  $B$  are constants to be determined from the boundary conditions. From  $T = T_1$  for  $r = r_1$  and  $T = T_2$  for  $r = r_2$ , it follows that

$$A = \frac{T_1 - T_2}{r_2 - r_1} r_1 r_2 \quad \text{and} \quad B = \frac{r_2 T_2 - r_1 T_1}{r_2 - r_1} \quad (11)$$

Eq. 10 becomes

$$T = \frac{T_1 - T_2}{r_2 - r_1} \frac{r_1 r_2}{r} + \frac{r_2 T_2 - r_1 T_1}{r_2 - r_1} \quad (12)$$

which represents the temperature  $T$  at any distance  $r$  from the center of the spherical shell.

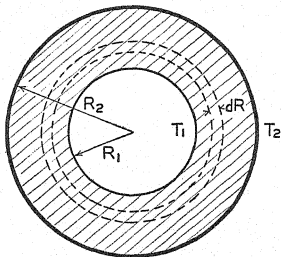


FIG. 14.—Conduction through spherical shell.

An electrical heater may be placed in the spherical cavity represented by Fig. 14 and if power is supplied at a constant rate until steady conditions are reached, the equations of the preceding paragraph are applicable. By differentiating Eq. 12 to obtain  $\partial T / \partial r$  an expression for the energy supplied per second  $EI / J$  (cal./sec.) may be found,

$$\frac{EI}{J} = -kA' \frac{\partial T}{\partial r} = k4\pi r^2 \frac{T_1 - T_2}{r_2 - r_1} \cdot \frac{r_1 r_2}{r^2} \quad (13)$$

Hence the conductivity of the shell may be calculated by this electrical method from

$$k = \frac{EI(r_2 - r_1)}{4\pi J r_1 r_2 (T_1 - T_2)} \quad (14)$$

### Cylinder, radial flow

In a much-used method for measuring thermal conductivity, energy is supplied electrically to a straight wire surrounded by a concentric cylindrical shell of the material being tested. To find an expression for  $k$  measured by this method we proceed as above, first getting an equation for the temperature  $T$  at a distance  $r$  from the axis of the cylinder.

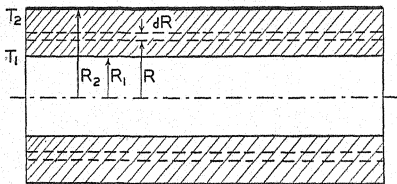


Fig. 15.—Conduction through cylindrical shell.

From Fig. 15 it is apparent that the energy leaving the cylindrical surface per second is

$$\frac{Q}{t} = -k2\pi r l \left( \frac{\partial T}{\partial r} \right) = \text{constant} \quad (15)$$

By integration

$$T = A \log_e r + B \quad (16)$$

The constants of integration  $A$  and  $B$  are determined from the boundary condition; for  $r = r_1$ ,  $T = T_1$  and for  $r = r_2$ ,  $T = T_2$ . It follows that

$$A = \frac{T_1 - T_2}{\log_e \frac{r_1}{r_2}} \quad \text{and} \quad B = \frac{T_2 \log_e r_1 - T_1 \log_e r_2}{\log_e \frac{r_1}{r_2}} \quad (17)$$

Substitution of these values in Eq. 16 gives

$$T = \frac{T_1 - T_2}{\log_e \frac{r_1}{r_2}} \log_e r + \frac{T_2 \log_e r_1 - T_1 \log_e r_2}{\log_e \frac{r_1}{r_2}} \quad (18)$$

For a steady state, the heat loss in calories per second per unit length of cylinder is

$$\frac{EI}{Jl} = -2\pi rk \frac{\partial T}{\partial r} = 2\pi rk \frac{T_1 - T_2}{\log_e r_2 - \log_e r_1} \cdot \frac{1}{r} \quad (19)$$

Hence the conductivity of the cylinder may be determined from

$$k = \frac{EI \log_e \frac{r_2}{r_1}}{2\pi Jl(T_1 - T_2)} \quad (20)$$

## Convection

### Coefficient of convection

The heat exchange between a fluid and a wall of uniform temperature is proportional to the area of contact, the difference between the two temperatures and the time,

$$Q = cA(T - T_w)t \quad (21)$$

The constant  $c$  is called the coefficient of convection. The heat transfer depends upon more factors than the area, temperature and time which appear explicitly in Eq. 21. In this crude expression there are lumped together in  $c$  all such implicit factors as relative velocity; region of flow (turbulent or laminar); density, specific heat and conductivity of the liquid; roughness and form of the wall, . . . etc.

Builders of heat apparatus have long used gross coefficients of convection, determined previously by experiment for apparatus of a similar type. This leads to satisfactory results under the limitations on  $(T - T_w)$  and on  $dQ/dA$  met with in practice (for liquids which do not change state). In the attempt to calculate  $c$  as a function of the multitude of

factors previously neglected, the first step was the development of empirical formulas expressing the influence of velocity on  $k$ . These had various forms:  $c = c_0 \sqrt[3]{r}$ ;  $c = c_0' \sqrt{v}$ ;  $c = c_0'' + c_1 \sqrt{v}$ —each based on a comparatively narrow range of observations, none of them general.

The application of dimensional analysis to the problem by Nüsselt, Reitschel and Grober led to formulas in which  $v$  entered to the  $\sim 0.8$  power for turbulent circulation parallel to a wall and to the  $\sim 0.6$  power for circulation perpendicular to a wall.

### Lévêque formula for $c$

Lévêque developed a binomial equation which takes account of the effects of velocity, length and diameter on  $c$  in the practical case of fluid flow in a tube. A differential equation is written for turbulent flow, treating the velocity of the fluid at a particular point as resulting from a longitudinal velocity and a vortex velocity. The latter changes sign with time, its average value being zero. To the term

$v_1 \frac{dT}{dl}$ , which represents the effect of longitudinal velocity,

there is added a term  $v_r' \frac{dT}{dr}$  to take account of transverse vortices,

$$v_1 \frac{\partial T}{\partial l} + v_r' \frac{\partial T}{\partial r} = \frac{s}{k\rho} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (22)$$

where  $s$  is the specific heat,  $k$  the conductivity and  $\rho$  the density of the liquid.

As a first approximation we may take  $v_r' = 0$  at the wall ( $r = R$ ), and  $v_r' = -hv_1$  for  $r = 0$ . The constant  $h$  depends upon the roughness of the wall, diameter of the tube, its inclination, conditions of turbulence at the entrance and the nature of the fluid. At a point remote from the wall,

$$v_r' \frac{dT}{dr} = hv_1 \frac{T - T_w}{R}$$

The approximate equation for turbulent flow becomes

$$v_1 \frac{dT}{dl} + hv_1 \frac{T - T_w}{R} = \frac{s}{k\rho} \left( \frac{\partial^2 T}{\partial r^2} - \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (23)$$

Assuming  $v$  to be an elliptic function of  $r$ , L       obtained an expression for the average coefficient of convection  $\bar{c}$ ,

$$\bar{c} \frac{d}{s} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{d}{l}} \sqrt{\frac{vk\rho d}{s}} + \frac{h}{2} \frac{vk\rho d}{s} \quad (24)$$

To show the influence of velocity alone, this can be put in the form

$$c = av^{0.5} + bv \quad (25)$$

The curve of  $c \frac{d}{s}$  against  $\frac{(vk\rho d)}{s}$  is concave upward, and approximates well the experimental curve—better than does N      's formula  $c = c_0 v^{0.786}$ . At small velocities the term in  $v$  (accelerated conduction) predominates in Eq. 24, while for large velocities the term in  $v$  (turbulent transport) surpasses it. The density of the fluid (determined by pressure if it is a gas) influences the relative importance of the two terms. The first varies as  $\sqrt{\rho}$  (or as  $\sqrt{p}$ ), the second varies as  $\rho$  (or as  $p$ ). As the density increases,  $c$  approaches  $bv$ .

### Methods of improving convection coefficients

The methods at our disposal for improving the values of convection coefficients will be considered briefly, in outline form.

- (a) Devices to improve direct transport of heat by vortices:
  - Large specific heat of liquid, or conductivity for gas (increase with temperature).
  - High velocity of circulation (increases with temperature).
  - Choice of liquid whose density and specific heat are as large as possible.
- (b) Devices concerned with turbulence only:
  - Choice of viscous fluid.
  - Use of tubes of small diameter having rough surfaces.
  - Eddies at entrance of canals, bends in circuit.

- (c) Devices concerned with accelerated conduction only:  
 Choice of fluid having good conductivity, yet having high viscosity.  
 Choice of short tubes. (This is generally not feasible since it would necessitate too many tubes connected in parallel.)
- (d) Devices which improve vaporization:  
 Removal from wall of bubbles of vapor which have poor conductivity, by giving liquid large velocity or vibrating wall.
- (e) Devices which improve condensation:  
 Limit thickness of condensed liquid which forms a poorly-conducting sheath, by decreasing that dimension of the tube which is parallel to the flow.  
 Decrease the amount of condensate which first tubes deliver to lower tubes.  
 Assure equipartition of fresh vapor among the tubes.
- (f) Devices which improve natural convection:  
 Attain greatest possible value of  $T - T_w$  to increase velocity of liquid  
 Reduce vertical dimensions of heating surfaces.

In general these considerations suggest the desirability of circulating permanent fluids (liquids or gases) if possible under pressure, always at high velocity, in narrow canals. These should not be numerous, hence must be long, to provide a large total surface.

## Radiation

### Mutual radiation of two surfaces

In describing the reflection of heat, e.g., in a furnace, one is tempted to make the angle of reflection equal to the angle of incidence—a false analogy with the optics of polished surfaces. Energy radiated from a mat surface in any direction varies as the cosine of the angle formed by that direction and the normal to the surface (Lambert's law). It is independent of the angle of incidence of the radiation received.

The heat exchange between two finite surfaces by mutual radiation is, by the Stefan-Boltzmann law, given by

$$Q = \sigma \iiint \frac{\cos \varphi \cos \theta}{\pi} (T_1^4 - T_2^4) dS = \sigma S \bar{\mu} (T_1^4 - T_2^4) \quad (26)$$

The factor  $S\bar{\mu}$  may have either form,

$$S\bar{\mu} = S_1 \left\{ \iint_{S_2} \frac{\cos \varphi d\theta}{\pi} \right\}_{\text{av.}} = S_2 \left\{ \iint_{S_1} \frac{\cos \varphi d\theta}{\pi} \right\}_{\text{av.}} \quad (27)$$

The  $\mu$ -factors (of which  $\bar{\mu}$  is the average) are determined from the projection on one element of the solid angle through which it "sees" the other (Fig. 16). If this angle is a hemisphere,  $\mu = 1$ .

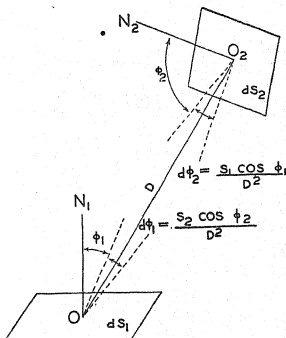


FIG. 16.—Mutual radiation between two surfaces.

### Radiation and temperature

Exchange of heat by radiation is governed by a law in  $T_1^4 - T_2^4$ . Heat transferred by other methods (conduction and convection) follows at least approximately a law in  $T_1 - T_2$ .

The quantity  $T_1^4 - T_2^4$  can be put in the form of a function of  $T_1 - T_2$  and one of the two factors:  $T_1$  or  $T_2$ ,

$$\begin{aligned} T_1^4 - T_2^4 &= f(T_1 - T_2, T_1) \text{ or} \\ T_1^4 - T_2^4 &= 4T_1^3(T_1 - T_2) - 6T_1^2(T_1 - T_2)^2 \\ &\quad + 4T_1(T_1 - T_2)^3 - (T_1 - T_2)^4 \quad (28) \end{aligned}$$



The exchange of heat is seen to depend not only on the difference between the temperatures of the two surfaces, but also on the value of at least one of these temperatures.

By considering the variation of  $T_1^4 - T_2^4$ , first as a function of  $T_1 - T_2$  then as a function of  $T_1$ , we are led to several generalizations in the following cases.

- (a) Hot and cold temperatures not comparable ( $\Delta T \sim 1000^\circ\text{C}.$ ):

The heat radiated depends on  $T_1^4$ , being practically independent of  $T_2$ , even though  $T_2$  may not be, properly speaking, a "cold" temperature. This is the case of boiler furnaces where  $T_1$  the temperature of the grate or radiating carbon particles is  $1400 + 273^\circ\text{K}.$ , and the temperature of the receiving surfaces (tubes) is  $300 + 273^\circ\text{K}.$  if they are clean, or  $500 + 273^\circ\text{K}.$  if they are covered with soot and scale.

- (b) Hot and cold temperatures comparable ( $\Delta T$  several hundred degrees):

The influence of  $T_1 - T_2$  (hence of  $T_2$ ) can no longer be neglected compared to that of  $T_1$ . The heat transfer, much diminished, depends on the cold temperature as well as on the hot. This is the case with certain furnaces, heat exchangers, and condensers.

- (c) Hot and cold temperatures approximately equal ( $\Delta T \sim 50^\circ$ ):

As  $T_1 - T_2 \rightarrow 0$ , the effect of  $T_1 - T_2$  is preponderant and even eclipses that of  $T_1$  at low temperatures. The heat radiated follows then a simple law in  $T_1 - T_2$ . This is the case of the walls in a building, hot water radiators, constant-temperature baths, etc.

Newton's law,  $Q \propto (T_1 - T_2)$ , applies only to temperature differences which are very small.

## Summary

Heat is transmitted by conduction, convection and radiation, of which the latter is the most important at high temperature. Newton's law is applicable only when temperature differences are very small. The conductivities of materials are usually measured with specimens in geometrically-simple forms: rectangular prism, sphere, cylinder. The equation representing heat conduction in such a simple solid is derived by: (1) writing the equation for the flow of heat through an element of area, (2) integrating this to find the temperature as a function of a linear distance and (3) substituting this value of  $T$  in the Fourier equation, Eq. 8.

## References

- Cammerer, J. S. "Die konstruktiven Grundlagen des Wärme und Kälteschultzes," *Wohn- und Industriebau*, Berlin: J. Springer, 1936.
- Fourier, J. *The Analytical Theory of Heat*, London: Cambridge U. Press, 1878.
- Griffiths, E. "Heat Insulating Materials," *J. Sci. Instruments*, 15, 117-121 (1938).
- McAdams, W. H. *Heat Transmission*, New York: McGraw-Hill, 1933.
- Roszak, C. and Veron, M. *Nouvelles études sur la chaleur*, Paris: Dunod, 1929.
- Schack, A. *Industrial Heat Transfer*, New York: J. Wiley, 1933.

## Problems

1. In measuring the conductivity of cork in the apparatus of Fig. 11, the heater has faces of 200 cm.<sup>2</sup> area and takes a current of 0.46 amp. from a 6 v battery. Thermocouples in the cork read a temperature difference of 50°C. between points 5 cm. apart on the horizontal axis. Calculate the thermal conductivity of the cork.
2. Derive an equation for converting a conductivity of  $X$  cal. sec.<sup>-1</sup> cm.<sup>-1</sup> deg.<sup>-1</sup> C. to B.t.u. hr.<sup>-1</sup> ft.<sup>-2</sup> for a temperature gradient of 1°F. per inch.
3. A room has 4 windows each of area 2 m.<sup>2</sup> The glass is 0.25 cm. thick. What weight of coal (heat of combustion 7,000 cal. gm.<sup>-1</sup>) need be burned per day to maintain a temperature of 20°C. within when the outdoor temperature is -10°C.? Comment on your answer.

4. Two thin concentric spherical shells of radii 5 cm. and 15 cm. have their annular cavity filled with charcoal. When energy is supplied at the steady rate of 10.79 w. to a heater at the center a temperature difference of  $50^{\circ}\text{C}$ . is observed between the spheres. Find the thermal conductivity of charcoal.
5. A steam pipe has an outer diameter of 10 cm. and a surface temperature of  $150^{\circ}\text{C}$ . It is covered with a layer of asbestos 2.5 cm. thick whose outer surface is at  $25^{\circ}\text{C}$ . If the thermal conductivity of the asbestos is  $0.00040 \text{ cal. cm.}^{-1} \text{ deg.}^{-1} \text{ C. sec.}^{-1}$ , how much heat is lost per minute from a 1 meter section of the pipe?
6. A wire 1 mm. in diameter having a resistance of 0.1 ohm/cm. forms the axis of a gas-filled tube 4 cm. in diameter. A current of 0.25 amp. produces a difference in temperature of  $30^{\circ}\text{C}$ . between wire and tube. Calculate the thermal conductivity of the gas.
7. Heat is conducted through a slab composed of parallel layers of two different conductivities, 0.32 and 0.14 (c.g.s. units), and of thicknesses 3.6 and 4.2 cm. respectively. The temperatures of the outer faces of the slab are  $96^{\circ}\text{C}$ . and  $8^{\circ}\text{C}$ . Find the temperature gradient in each portion.
8. A constant-temperature water bath is held in a copper tank 0.2 mm. thick surrounded by celotex ( $k = 0.00068 \text{ watts in.}^{-1} \text{ deg.}^{-1} \text{ F.}$ ) 2 cm. thick and supported by a 1-cm. pine board. The outer surface of the wood is painted with aluminum paint which, in contact with still air, has a radiation constant of  $0.0024 \text{ w. in.}^{-2} \text{ deg.}^{-1} \text{ F.}$  Calculate the thermal conductivity of the walls per square meter.
9. The water bath of Prob. 8 is in the form of a 50-cm. cube, open at the top. If the heat loss from the surface of the water is  $2.3 \text{ w./in.}^2$ , what is the power (approximate) which must be supplied to a heater to keep the bath at  $160^{\circ}\text{F}$ . in a room of temperature  $72^{\circ}\text{F}$ .?
10. Express Eq. 6 in cylindrical coördinates.
11. Express Eq. 6 in spherical coördinates.

## CHAPTER III

# Thermoelectricity<sup>1</sup>

### Introduction

In 1821 Seebeck<sup>2</sup> discovered that an electric current flows continuously in a closed circuit of two dissimilar metals when their junctions are maintained at different temperatures (Fig. 17). In the early investigations of thermoelectric effects the results were expressed more qualitatively than quantitatively, because the relations between the measurable quantities in an electric circuit were not well known at the time. (The relation between the current and the electromotive force in an electric circuit was first clearly stated by Ohm in 1826.<sup>3</sup>)

A pair of electrical conductors so joined as to produce a thermal e.m.f. when the junctions are at different temperatures is known as a thermocouple. The resultant e.m.f. developed by the thermocouples generally used for measuring temperatures varies from about 1 to 7 millivolts when the temperature difference between the junctions is 100°C.

### Sign convention

If in a simple thermoelectric circuit, Fig. 17, the current flows from metal *A* to metal *B* at the colder junction, *A*

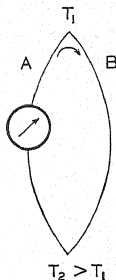


FIG. 17.—Simple thermoelectric circuit.

<sup>1</sup> Quoted largely from W. F. Roeser, *J. Applied Physics*, 11, 388 (1940).

<sup>2</sup> T. J. Seebeck, *Gilb. Ann.*, 73, 115, 430 (1823); *Pogg. Ann.*, 6, 1, 133, and 253 (1826).

<sup>3</sup> G. S. Ohm, *Schweigger's J.*, 46, 137 (1826).

will be referred to as thermoelectrically positive to  $B$ . In determining or expressing the e.m.f. of a thermocouple as a function of the temperature, one junction is maintained at some constant reference temperature, such as  $0^{\circ}\text{C.}$ , and the other is at the temperature corresponding to the e.m.f. The order in which the metals are named and the sign of the numerical value of the e.m.f. will be used to indicate which of the metals is positive to the other at the junction which is at the reference temperature. For example, if in Fig. 17,  $T_1$  is the reference temperature and the current flows in the direction indicated, the e.m.f. of thermocouple  $AB$  will be positive, and the e.m.f. of thermocouple  $BA$  will be negative.

### Thermoelectric laws

As a result of a large number of investigations of thermoelectric circuits in which accurate measurements were made of the e.m.f., current and resistance, several facts have been established. These facts or laws can be reduced to three fundamentals.

(i) *The law of the homogeneous circuit.* An electric current cannot be sustained in a circuit of a single homogeneous metal, however varying in section, by the application of heat alone. No theoretical derivation of this principle has been presented. It has been claimed from certain types of experiments that a nonsymmetrical temperature gradient in a homogeneous wire produces a measurable thermoelectric emf. However, the weight of evidence indicates that any e.m.f. observed in such a circuit is to be attributed to the effects of local inhomogeneities. (As a matter of fact, at the present time any current detected in such a circuit when the wire is heated in any way whatever, is taken as evidence that the wire is inhomogeneous.)

We shall accept, as an experimental fact, the general statement that the algebraic sum of the e.m.f.'s in a circuit of a single homogeneous metal however varying in section and temperature is zero. As a consequence of this fact, if one

junction of two dissimilar homogeneous metals is maintained at a temperature  $T_1$  and the other junction at a temperature  $T_2$ , the thermal e.m.f. developed is independent of the temperature gradient and distribution along the wires.

(ii) *The law of intermediate metals.* This law will be stated in several ways, and although the statements may appear different, they are really equivalent.

One statement of the law is: *The algebraic sum of the thermoelectromotive forces in a circuit composed of any number of dissimilar metals is zero, if all of the circuit is at uniform temperature.* This law follows as a direct consequence of the second law of thermodynamics (Chap. XII), because if the sum of the thermoelectromotive forces in such a circuit were not zero, a current would flow in the circuit. If a current should flow in the circuit, some parts of it would be heated and other parts cooled, which would mean that heat was being transferred from a lower to a higher temperature without the application of external work. Such a process is a contradiction of experience. Therefore we conclude that the algebraic sum of the thermoelectromotive forces is zero in such a circuit.

Combining this law with that for a homogeneous circuit, it is seen that in any circuit, if the individual metals between junctions are homogeneous, the sum of the thermal e.m.f.'s will be zero provided only that the junctions of the metals are all at the same temperature.

Another way of stating the law of intermediate metals is: *If in any circuit of solid conductors the temperature is uniform from point P through all the conducting matter to point Q, the algebraic sum of the thermoelectromotive forces in the entire circuit is totally independent of this intermediate matter and is the same as if P and Q were put in contact (Fig. 18).*

Thus it is seen that a device for measuring the thermoelectromotive force may be introduced into a circuit at any point without altering the resultant e.m.f. provided that the junctions which are added to the circuit by introducing the

device are all at the same temperature. It is also obvious that the e.m.f. in a thermoelectric circuit is independent of the method employed in forming the junctions as long as all of the junction is at a uniform temperature, and the two wires make good electrical contact at the junction, such as obtained by welding or soldering.

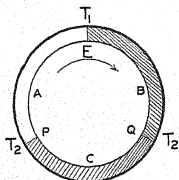


FIG. 18.— $E_{ABC} = E_{AB}$ .

A third way of stating the law of intermediate metals is: *The thermal e.m.f. generated by any thermocouple AB with its junction at any two temperatures  $T_1$  and  $T_2$ , is the algebraic sum of the e.m.f. of a thermocouple composed of A and any metal C and that of one composed of C and B, both with their junctions at  $T_1$  and  $T_2$ , or  $E_{AB} = E_{AC} + E_{CB}$  (Fig. 19).*

From this statement of the law it is seen that if the thermal e.m.f. of each of the metals A, B, C, D, etc. against some reference metal is known, then the e.m.f. of any combination of these metals can be obtained by taking the algebraic differences of the e.m.f.'s of each of the metals against the reference metal. Investigators tabulating thermoelectric data have employed various reference metals such as mercury, lead, copper and platinum. At present it is customary to use platinum because of its high melting point, stability, reproducibility, and freedom from transformation points.

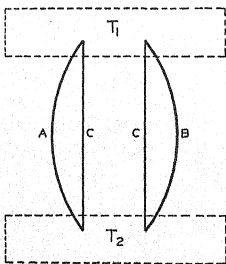


FIG. 19.— $E_{AB} = E_{AC} + E_{CB}$ .

(iii) *The law of successive or intermediate temperatures.*

*The thermal e.m.f. developed by any thermocouple of homogeneous metals with its junctions at any two temperatures  $T_1$  and  $T_2$  is the algebraic sum of the e.m.f. of the thermocouple*

with one junction at  $T_1$  and the other at any other temperature  $T_2$  and the e.m.f. of the same couple with its junctions at  $T_2$  and  $T_3$ . (Fig. 20). Considering the thermocouple as a reversible heat engine and applying the laws of thermodynamics to the circuit, it will be shown (p. 55) that

$$E = \int_{T_1}^{T_3} \phi dT$$

from which it follows that

$$E = \int_{T_1}^{T_2} \phi dT + \int_{T_2}^{T_3} \phi dT$$

This law is frequently invoked in the calibration of thermocouples and in the use of thermocouples for measuring temperatures.

The above are all the fundamental laws required in the measurement of temperatures with thermocouples. They may be and frequently are combined and stated as follows: The algebraic sum of the thermoelectromotive forces generated in any given circuit containing any number of dissimilar homogeneous metals is a function only of the temperatures of the junctions. It is seen then that if all but one of the junctions of such a circuit are maintained at some constant reference temperature, the e.m.f. developed in the circuit is a function of the temperature of that junction alone. Therefore, by proper calibration such a device may be used to measure temperatures.

It should be pointed out that none of the fundamental laws of thermoelectric circuits, which make it possible to utilize thermocouples in the measurement of temperatures,

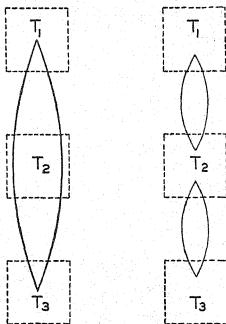


FIG. 20.— $|E|_{T_1}^{T_3} = |E|_{T_1}^{T_2} + |E|_{T_2}^{T_3}$ .



depends upon any assumption whatever regarding the mechanism of interconversion of heat and electrical energy, the location of the e.m.f.'s in the circuit, or the manner in which the e.m.f. varies with the temperature. All of these laws have been established experimentally beyond a reasonable doubt and in order that temperatures may be measured by this method the laws must be accepted in spite of any lack of rigor that may appear in any of the thermodynamic derivations.

### Historical investigation

Although a knowledge of the location of the e.m.f.'s in a thermoelectric circuit, and the mechanism by which heat is converted into electrical energy, is not required in order to measure temperatures with thermocouples, any information available on these subjects may be used advantageously in studying the characteristics of thermocouples and their behavior during use. Various theoretical and experimental investigations of thermoelectric circuits give us the location of the e.m.f.'s in such a circuit, and the relation between these e.m.f.'s, but they have not yielded a satisfactory explanation of the mechanism by which heat is converted into electrical energy or of the manner in which the e.m.f. varies with temperature, except empirical relations.

In 1834 Peltier<sup>4</sup> found that when a current is passed across the junction of two dissimilar metals in one direction heat is absorbed and the junction cooled, and that when current is passed in the opposite direction the junction is heated. Peltier and others observed that for a given current the rate of absorption or liberation of heat at the junction of two dissimilar metals depends upon the thermoelectric power  $dE/dT$  of the two metals and is independent of the form and dimensions of the metals at the junction. In 1853 Quintus Icilius showed that the rate at which heat is absorbed or

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<sup>4</sup> J. C. A. Peltier, *Ann. chim. Phys. 2nd ser.*, 56, 371 (1834).

generated at a junction of two dissimilar metals is proportional to the current. This heating or cooling effect discovered by Peltier should not be confused with the Joule heating effect which, being proportional to  $I^2R$ , depends upon the dimensions of the conductor and does not change sign when the current is reversed.

Inasmuch as heat is absorbed when current flows up a potential gradient and heat is generated when the current flows down a potential gradient, the heating or cooling effect at a junction of two dissimilar metals (being proportional to the current) is evidence that the junction is the seat of an e.m.f. If we let  $P$  be the rate at which heat (in joules per second or in watts) is generated or absorbed when a current of one ampere flows across a junction, then  $P$  is the Peltier coefficient of the junction (in watts per ampere) or more simply the Peltier e.m.f. (in volts). The direction and magnitude of this e.m.f. depend upon the metals which form the junctions and upon the temperature.

In 1851, W. Thomson<sup>5</sup> (later Lord Kelvin) concluded from thermodynamic reasoning and the then known characteristics of thermocouples that the reversible absorption of heat at the junctions of dissimilar metals was not the only reversible heat effect in a thermoelectric circuit. In brief he reasoned as follows:

(1) Assuming that the Peltier e.m.f.'s represent the only reversible effects in a simple thermoelectric circuit, the resultant e.m.f.  $E$  in the circuit is given by

$$E = P_2 - P_1 \quad (1)$$

where  $P_1$  is the Peltier e.m.f. of the junction which is at temperature  $T_1$ ; and  $P_2$  is the Peltier e.m.f. of the junction which is at temperature  $T_2$ .

(2) Neglecting the effect of thermal conduction (an irreversible process) and considering the thermocouple as

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<sup>5</sup> W. Thomson, *Proc. Roy. Soc. Edin.* December 15, 1851.

a reversible heat engine with a source at the temperature  $T_2$  in degrees Kelvin and a sink at the temperature  $T_1$  we have as a consequence of the second law of thermodynamics

$$\frac{P_2}{T_2} = \frac{P_1}{T_1} = 0 \quad (2)$$

or

$$\frac{(P_2 - P_1)}{P_1} = \frac{(T_2 - T_1)}{T_1} \quad (3)$$

which combined with Eq. 1 gives

$$E = \frac{P_1(T_2 - T_1)}{T_1} \quad (4)$$

It would follow therefore that if one junction were maintained at a constant temperature  $T_1$ ,  $P_1$  would be constant and the e.m.f.  $E$  would be proportional to  $(T_2 - T_1)$ . It had been definitely shown by a number of investigators that  $E$  was not proportional to  $(T_2 - T_1)$ . Thomson therefore concluded that the Peltier effects were not the only reversible heat effects in such a circuit and that there must be a reversible absorption of heat due to the flow of current through that part of the conductors in which there is a temperature gradient.

In 1854 Thomson<sup>6</sup> succeeded in showing experimentally that in certain homogeneous metals, heat is absorbed when an electric current flows from colder to hotter parts. In certain other metals the opposite of this effect occurs, and in still other metals, the effect is too small to be detected by the methods used. This heating or cooling effect, called the Thomson effect, is reversible in the thermodynamic sense, i.e., it is a transformation which can be made to proceed in the opposite sense by only infinitesimal change in one of the conditions determining the transformation. The Thomson effect, being reversible and occurring only where there is a

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<sup>6</sup> W. Thomson, *Proc. Roy. Soc. Lon.* VII May, 1854; *Phil. Mag.* July, 1854.

temperature gradient in a metal, is entirely distinct from the irreversible Joule heating.

The reversible absorption of heat in a homogeneous conductor has the same effect as if an e.m.f. existed in the temperature gradient. The direction and magnitude of this e.m.f. between any two points depend upon the metal, the temperature, and the temperature difference between the two points. If in any metal we let  $\sigma$  equal the rate at which heat is absorbed or generated per unit difference of temperature when a current of one ampere flows, then the total

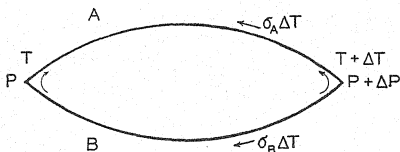


FIG. 21.—The location of the e.m.f.'s in a thermoelectric circuit.

e.m.f. between any two points at temperatures  $T_1$  and  $T_2$  is given by

$$\int_{T_1}^{T_2} \sigma dT$$

In a simple thermoelectric circuit of two metals  $A$  and  $B$ , Fig. 21, there exist four separate and distinct e.m.f.'s: the Peltier e.m.f.'s at the two junctions and the Thomson e.m.f.'s along that part of each wire which lies in the temperature gradient. The identity of the individual e.m.f.'s can be established only by observations of the reversible heat effects. The Thomson e.m.f. will be considered positive if heat is generated when current flows from the hotter to the colder parts of the conductor and negative if the reverse occurs.

### Thermodynamic theory

Thomson took into consideration the reversible heat effects in the temperature gradient of the conductors, (Thom-

son effects), as well as those at the junctions, (Peltier effects), and applied the laws of thermodynamics to the thermoelectric circuit. A complete discussion of this application together with the hypothesis involved is given in the original paper by Thomson.<sup>7</sup>

Consider a simple thermoelectric circuit of two metals  $A$  and  $B$ , Fig. 21, and let  $P$  and  $P + \Delta P$  be the Peltier e.m.f.'s of the junctions at temperatures  $T$  and  $T + \Delta T$  in degrees Kelvin, respectively, and let  $\sigma_A$  and  $\sigma_B$  be the Thomson e.m.f.'s per degree along conductors  $A$  and  $B$  respectively. Let the metals and temperatures be such that the e.m.f.'s are in the directions indicated by the arrows. The resultant e.m.f.,  $\Delta E$ , in the circuit is given by

$$\Delta E = P + \Delta P - P + \sigma_A \Delta T - \sigma_B \Delta T \quad (5)$$

$$\Delta E = \Delta P + (\sigma_A - \sigma_B) \Delta T \quad (6)$$

or in the limit

$$\frac{dE}{dT} = \frac{dP}{dT} + (\sigma_A - \sigma_B) \quad (7)$$

By virtue of the second law of thermodynamics  $\Sigma Q/T = 0$  for a reversible process. If then we regard the thermocouple as a reversible heat engine and pass a unit charge of electricity around the circuit, we obtain by considering only the reversible effects

$$\frac{q(P + \Delta P)}{T + \Delta T} - \frac{qP}{T} + \frac{q\sigma_A \Delta T}{T + \frac{\Delta T}{2}} - \frac{q\sigma_B \Delta T}{T + \frac{\Delta T}{2}} = 0 \quad (8)$$

which may be written

$$\Delta \left( \frac{P}{T} \right) + \frac{(\sigma_A - \sigma_B) \Delta T}{T + \frac{\Delta T}{2}} = 0 \quad (9)$$

or in the limit

$$\frac{d}{dT} \left( \frac{P}{T} \right) + \frac{1}{T} (\sigma_A - \sigma_B) = 0 \quad (10)$$

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<sup>7</sup> W. Thomson, *Trans. Roy. Soc. Edin.*, 21, 123 (1857).

or

$$\sigma_A - \sigma_B = \frac{P}{T} - \frac{dP}{dT} \quad (11)$$

Eliminating  $(\sigma_A - \sigma_B)$  between Eq. 7 and Eq. 11 we have

$$P = T \frac{dE}{dT} \quad (12)$$

Substituting Eq. 12 in Eq. 10 we have

$$\sigma_A - \sigma_B = T \frac{d^2E}{dT^2} \quad (13)$$

From Eq. 12 it is seen that

$$E = \int_{T'}^T \frac{P}{T} dT = \int_{T'}^T \phi dT \quad (14)$$

which is the expression referred to earlier (p. 49).

The Peltier e.m.f. at the junction of any two dissimilar metals at any temperature can be calculated from Eq. 12 and measurements of the variation of the thermal e.m.f. with temperature. The magnitude of the e.m.f. existing at the junction of two dissimilar metals ranges from 0 to about 0.1 volt for the metals commonly used in temperature measurements. Although the thermoelectric theory as developed above does not enable us to determine directly the magnitude of the Thomson coefficient in any individual metal, the difference between the Thomson coefficients in two metals can be calculated from Eq. 13 and measurements of the variation in thermal e.m.f. with temperature. Various types of experiments indicate that the Thomson effect in lead is extremely small, if not zero, at ordinary atmospheric temperatures. Consequently some information regarding the magnitude of the Thomson coefficients in other metals at these temperatures can be determined if it is assumed that this coefficient is zero for lead. On this basis it is found that the Thomson coefficient at 0°C. in microvolts per °C. is -9

for platinum,  $-8$  for iron,  $+2$  for copper,  $-23$  for constantan,  $-8$  for Alumel,  $-2$  for 90Pt10Rh alloy and  $+9$  for Chromel-P.

In order to satisfy the assumptions involved in the application of the second law of the thermodynamics, it is necessary and sufficient to verify experimentally the relation

$$P = T \frac{dE}{dT} \quad (12)$$

and

$$\sigma_A - \sigma_B = T \frac{d^2E}{dT^2} \quad (13)$$

Inasmuch as the individual e.m.f.'s cannot be measured as such, we must depend upon calorimetric measurements of the heating and cooling effects. In order to measure these small reversible effects, it is necessary to separate them from the much larger irreversible Joule heating and the thermal conduction which take place in any experimental work of this nature. Practically all of the experimental work on this subject has been on the relation given by Eq. 12 because the reversible heating effects involved in it are in general much larger and more localized than those in Eq. 13.

We cannot integrate Eq. 12 or 13 and obtain a general relation between  $E$  and  $T$ , without some information on the manner in which  $P$  or  $\sigma$  varies with  $T$ . Experiments indicate that  $P$  and  $\sigma$  both depend upon  $T$  but the manner in which they vary with  $T$  has not been established either theoretically or experimentally with any degree of accuracy.

A number of hypotheses have been made as to the manner in which  $\sigma$  varies with the temperature and Eq. 13 then integrated. P. Q. Tait and others have suggested, on the basis of limited experimental evidence, that  $\sigma$  is proportional to  $T$ . If so, the thermoelectric power may be expressed as a linear equation

$$\frac{dE}{dT} = b + 2cT \quad (15)$$

and for practical purposes the e.m.f. of a thermocouple may be expressed by

$$E = a + bt + ct^2 \quad (16)$$

where  $t$  is the centigrade temperature of the measuring junction, the reference junction being kept at some constant temperature. While this equation may be considered as applicable to most thermocouples of practical importance, there are many materials whose e.m.f.-temperature curves cannot be so simply represented. Equations relating  $E$  and  $T$ , based on any particular hypothesis regarding the functional relation between  $\sigma$  and  $T$ , represent the experimentally determined values of  $E$  and  $T$  only over limited temperature ranges. Consequently the relation between  $E$  and  $T$  for any pair of metals must be determined experimentally and corresponding values given by tables or empirical relations for limited temperature ranges.

Later theories of thermoelectricity may be divided into two general classes: (1) those in which attempts are made to avoid the hypothesis made by Thomson, and (2) those in which the theory as developed by Thomson is accepted as far as it goes, and attempts are made to derive a reversible mechanism or process for converting heat into electrical energy by the application of the electron theory of metals. The theories in the first general class have added little, if anything, to our knowledge of thermoelectricity. The assumptions involved in most of these appear more objectionable than the one made by Thomson. The relations derived between the quantities involved are either equivalent to or less useful than those derived by Thomson.

### Electron theory

The existence of the Peltier and Thomson e.m.f.'s in a thermoelectric circuit may be deduced, qualitatively at least, from the electron theory of metals, but the uncertainties in the quantities involved are so large that we cannot determine



whether the theories are in agreement with experimental data or not. The most that can be claimed for the more complete of these theories at the present time is that they give the order of magnitude of the various effects for certain metals.

### Electron theory of thermoelectricity

Electron theories of thermoelectricity are of interest in providing us with a simple (although incomplete) picture of the possible mechanism of thermoelectricity. A metal may be regarded as possessing conduction electrons having one

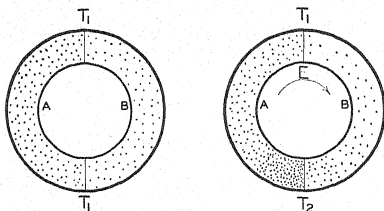


FIG. 22.—Electron density as the source of thermoelectromotive force.

degree of freedom of motion in the metal. In different metals these electrons have different concentrations and different average velocities of thermal agitation. If two metals are placed in contact (Fig. 22) there is a diffusion of electrons across the interface. As soon as sufficient negative charge is transferred to produce an e.m.f. across the boundary which repels the arrival of more electrons, a dynamic balance is attained with no further net diffusion.

If metals *A* and *B* are brought into contact at another point to form a complete circuit, and the two junctions are kept at the same temperature, the thermal e.m.f.'s at the junctions are equal and opposite. No net flow of electrons occurs. If, however the junctions are maintained at different temperatures, the electron concentrations (or pressures)

differ and a steady flow occurs. Heat energy is transformed into electrical energy.

A theory developed by Lorentz and J. J. Thomson gives the e.m.f. in terms of the electron concentrations,  $n_1$  and  $n_2$ , in the two metals, the gas constant  $R$  and Faraday's constant  $F$ :

$$E = \frac{R}{F} \log \frac{n_1}{n_2}.$$

This is not particularly useful, since the electron concentrations are unknown.

### Quantum theory of thermoelectricity

A quantum theory of metals seeks to explain and predict quantitatively the values of their various thermal, electric and magnetic effects, including thermoelectricity. Exact results have been obtained only for isotropic (cubic) crystals at high temperatures (well above their Debye temperatures). While an ultimate understanding of thermoelectric phenomena probably lies in an extension of such investigations, so far quantum theory has added little information of practical value to that which can be obtained from general thermodynamic considerations.

### Summary

An e.m.f. is produced in a circuit of two or more dissimilar metals, or in a circuit of one metal, different parts of which are in dissimilar physical states, when one junction is heated or cooled relative to the remainder of the circuit. This phenomenon is due to several distinct effects of which the Peltier effect alone is important in thermoelectric pyrometry. Three simple relations have practical importance in the use of thermocouples:

- (1)  $E_{ABC} = E_{AB}$  (both ends of  $C$  at same temperature)
- (2)  $E_{AB} = E_{AC} + E_{CB}$  (for a given temperature difference)
- (3)  $|E|_{T_1}^{T_3} = |E|_{T_1}^{T_2} + |E|_{T_2}^{T_3}$  (for a given thermocouple)

A second degree equation is usually sufficient to express the dependence of thermal e.m.f. on temperature.

### References

- Bridgman, P. W. *The Thermodynamics of Electrical Phenomena in Metals*, New York: Macmillan, 1934. 200 pp.
- Nordheim, L. *Die Theorie der thermoelektrischen Effekte*, Paris: Hermann & Cie., 1934. 26 pp.
- Page, L. and Adams, N. I. *Principles of Electricity*, New York: Van Nostrand. pp. 218-228.
- Roeser, W. F. "Thermoelectric Thermometry," *J. Applied Physics*, **11**, 388 (1940).
- Thomson, W. "On the dynamical theory of heat . . .," *Trans. Roy. Soc. Edinburgh*, **21**, 123-171 (1854).

### Problems

1. Distinguish between the Peltier heat and the Joule heat.
2. What is meant by the term "specific heat of electricity" as applied to  $\sigma$ ?
3. The thermoelectric power as a function of temperature may be represented as a straight line for each of two metals,  $A$  and  $B$ , against platinum. On this diagram what is the geometrical interpretation of the neutral temperature for an  $AB$  thermocouple?
4. Define neutral temperature in several ways.
5. Describe how a current-carrying wire with a small thermocouple soldered to it might be used to measure (i) an alternating current, (ii) the standard current for a potentiometer, (iii) the pressure of gas in a vacuum system, (iv) the extent of eddy currents in a wind tunnel, (v) the wind speed outdoors.
6. By applying the second law of thermodynamics (Chap. XII) to an e.m.f.-charge diagram for a thermocouple, show (i) that  $\sum \frac{Q}{T} = 0$  and (ii) that  $P = T \frac{dE}{dT}$ .
7. Identify all thermal e.m.f.'s of a thermocouple as areas on the thermoelectric diagram (thermoelectric power vs. temperature) for the couple.
8. How are the Peltier and Thomson coefficients represented on the thermoelectric diagram?
9. Using the data of Table XII, construct a thermoelectric diagram for iron and constantan (each vs. lead). State how the amounts of heat absorbed or evolved in the different parts of the iron-constantan

circuit with its junctions at  $0^{\circ}$  and  $100^{\circ}\text{C}$ . and a current of 1 ampere are shown in the diagram.

10. Show that  $\sigma = T \tan \theta$ , where  $\theta$  is the slope of the  $P$  vs.  $T$  line in a thermoelectric diagram.
11. The ends of a 30-cm. metal rod of  $1 \text{ cm.}^2$  cross section are maintained at  $30^{\circ}$  and  $0^{\circ}\text{C}$ . The resistivity of the metal is 150 microhm cm. When a current of 0.05 amp. flows from the hot to the cold end the temperature gradient in the rod is unchanged. Find the Thomson coefficient for the metal.



## Thermoelectric Temperature Measurements

### Introduction

Seebeck's discovery of thermoelectricity was used as early as 1830 as a new method of pyrometry by Becquerel in his measurement of flame temperatures. With the development of suitable thermocouple materials, thermoelectric pyrometry has attained a degree of precision inferior only to that of resistance thermometry below  $900^{\circ}\text{C}.$ , while for higher temperatures it is the only sensitive and convenient electrical method.

A thermocouple pyrometer consists of three main elements:

1. The thermocouple, comprising: two dissimilar metals, usually wires; electrical insulation; and usually a protecting tube.

2. Leadwires to connect thermocouple and instrument.

3. An e.m.f.-measuring instrument, usually a potentiometer or millivoltmeter; with provision—which may be at the instrument, or elsewhere—for controlling or compensating for reference-junction temperature.

The choice of thermocouple materials is influenced by the relative importance of such desirable characteristics as:

1. Resistance to chemical and mechanical deterioration in the environment in which it is used.

2. Development of relatively large e.m.f.'s. Ideally, the Thomson e.m.f.'s should be oppositely directed in the two wires, and the wire showing the negative Thomson e.m.f. should be the positive element for the Peltier e.m.f. at the hot junction. The four e.m.f.'s are then additive.

3. A temperature-e.m.f. relation in which the e.m.f. increases continuously with increasing temperature over the range of use. To provide a large thermoelectric power and to insure freedom from reversal of e.m.f., the neutral temperature should be remote from the temperature range of use.

4. Constancy of calibration. This is largely dependent upon freedom from contamination and mechanical strains which introduce inhomogeneities in the thermocouple elements.

5. Reproducibility of couples. This is an important consideration in industrial uses to permit replacement of the couple without necessitating recalibration of the temperature scale of the indicating instrument.

### Base-metal thermocouples

The first four thermocouples listed in Table I are base-metal couples extensively used for temperature measurement and control in the laboratory and in industrial processes. They are characterized by relatively high e.m.f.'s (4 to 7 times that of Pt-PtRh thermocouple) which permits the use of more rugged and less expensive indicators if deflection-type instruments are used. They are comparatively inexpensive. They have e.m.f.-temperature curves which are approximately linear. This is a desirable characteristic since measurements at only a few temperatures establish the calibration curve for the thermocouple; in checking the couple, the per cent correction determined in rechecking a calibrated couple at one temperature applies to the whole range; and reference junction corrections involve merely the addition or subtraction of a temperature interval.

The maximum useful range of a given type of thermocouple depends on the accuracy and reproducibility demanded, on the protection provided, and on whether continuous or intermittent service is required. All base-metal thermocouples become inhomogeneous with use at high temperature. The e.m.f. of an inhomogeneous thermocouple depends not

only on the temperatures of the measuring junction and the reference junction but also on the temperature distribution throughout the inhomogeneous portions of the wires.

Tests on the stability of base-metal thermocouples have shown that heating for a long time in air causes the e.m.f. corresponding to a given temperature to increase, or the temperature corresponding to a given e.m.f. to decrease in the case of a chromel-alumel couple.<sup>1</sup> The effect on an iron-constantan thermocouple is just the reverse. Changes in a chromel-constantan thermocouple are small because the effects in the individual wires counteract each other. While chromel-alumel thermocouples are serviceable to 1200°C., a couple which is to be used for accurate measurements below 550°C. should not be subjected to the higher temperatures.

Thermocouples are commonly in the form of wires with welded junctions—"wire-type" thermocouples, or "pipe-type" in which one element surrounds the other. Approximately 80% of the chromel and alumel used in thermocouples is in no. 8 gauge wire, and 95% is in no. 6, 8, 11 and 14 gauge wire. Where there is no danger of contamination, base-metal thermocouples are used without protection tubes, electrical insulation being provided by threading the wires through porcelain insulators. Pipe-type iron-constantan thermocouples are made with the iron element surrounding the constantan and welded to it at the tip to form a closed tube. The elements are insulated along their lengths by asbestos windings. Thermocouples are used in molten non-ferrous metals without a welded junction, the elements being removable rods or wires drawn from spools in the handle of the pyrometer and twisted together before insertion in the molten bath.

Thermocouples are designed in special forms for a wide variety of practical temperature measurements. Operating temperatures of internal combustion engines are measured

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<sup>1</sup> A. I. Dahl, *J. Research Nat. Bur. Standards*, 24, 205 (1940).

by thermocouples clamped under the plugs in the form of flat rings or fixed in cavities in the cylinder block. The friction between two dissimilar metal surfaces has been studied by measuring their thermal e.m.f.<sup>2</sup> The surface temperature of brass wire drawn through a steel die is determined by making the die and wire elements of a thermocouple.<sup>3</sup> A thermocouple in the form of a hypodermic needle is used for measuring the temperature of foods, tires, plastics, etc.<sup>4</sup>

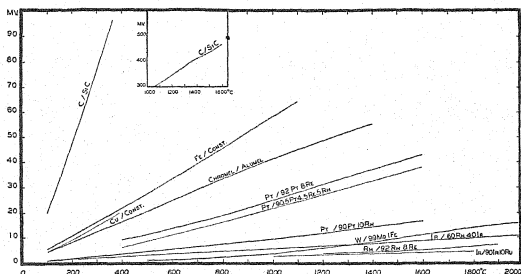


FIG. 23.—Temperature—e.m.f. characteristics of typical thermocouples.

Several types of base-metal thermocouples are used for high temperature measurements. 99Mo1Fe-W gives an e.m.f. of 16 mv. at 2000°C. and can be used to 2200°C. 75W25Mo-W has an e.m.f. of 5.8 mv. at 2570°C. and can be used to 3000°C.

### Rare-metal thermocouples

The Pt-90Pt10Rh thermocouple introduced by Le Chatelier is used extensively in measuring temperatures in the range 0° to 1550°C. It is used to define the international temperature scale in the range 660° to 1063°C. Some

<sup>2</sup> F. P. Bowden and L. Leben, *Nature*, **141**, 691 (1938).

<sup>3</sup> F. C. Thompson and H. G. Dyson, *Metallurgia*, **6**, 191 (1932).

<sup>4</sup> R. W. Brown, *J. Sci. Instruments*, **9**, 198 (1932).



American couples are made with a 87Pt13Rh alloy which gives a slightly higher e.m.f., largely to provide replacement couples for calibrated instruments already in use.

Both platinum and rhodium can be obtained with high purity. The Pt-PtRh couples have the primary advantages of reproducibility and long temperature range. High cost limits their use. The cost of long leads from the measuring junction to the reference junction of a Pt-PtRh thermocouple may be reduced by the use of compensating leads of dissimilar metals which together have the same thermoelectric properties as the thermocouple over the usual range of temperature of the thermocouple head. A copper wire is attached to the PtRh alloy wire, and a nickel-copper alloy wire to the platinum.

Rare-metal thermocouples are extremely sensitive to contamination by metallic vapors in a reducing atmosphere. They must be suitably protected if their calibration is to remain valid.

While Pt-PtRh thermocouples are the only rare-metal thermocouples in common use in this country, other types are coming into use in Germany to secure higher e.m.f. or higher temperature range or lower cost.<sup>5</sup> They do not appear to surpass the Pt-PtRh couple in reliability, and in some cases are inferior to base-metal couples. The Pallaplat couple (PtRh-AuPd5Pt) develops about five times the e.m.f. of a Pt-PtRh couple and costs half as much. However it has a shorter life and has a temperature maximum of 1000°–1200°C. Many metals have a larger e.m.f. in combination with platinum than does rhodium. Rhenium, osmium, tungsten and molybdenum have high e.m.f.'s and form workable platinum alloys up to 10 per cent by weight of added metal. Te-Pt and TeSb-Pt thermocouples are used for laboratory measurements in the ranges –200° to 100°

<sup>5</sup> A. Schulze, *Warme*, 62, 127 (1939); *Metalwissenschaft*, 18, 249, 271, 315 (1939); *Chem. Zeit.*, 62, 285 (1938).

H. Euler and K. Guthmann, *Arch. Eisenhüttenw.*, 9, 73 (1935).

and  $-200^{\circ}$  to  $300^{\circ}\text{C}$ . respectively. Other rare-metal thermocouples with their temperature limits are: PtRh5Re-PdAu . . . ,  $900$  to  $1250^{\circ}\text{C}$ .; Pd-60Fe40Cr, to  $1400^{\circ}\text{C}$ .; Pt-Pt5ReRh,  $1000$  to  $1600^{\circ}\text{C}$ .; Pt-Pt8Re to  $1800^{\circ}\text{C}$ .; Rh-Rh8Re to  $1900^{\circ}\text{C}$ .; Ir-60Rh40Ir to  $2000^{\circ}\text{C}$ .; and Ir-Ir10Ru to  $2000^{\circ}\text{C}$ .

### Non-metallic thermocouples

The carbon-graphite thermocouple is one of the oldest. Its e.m.f., less than 1 mv., is too small for practical use. Constantan-SiC and TaC-C couples have been used.<sup>6</sup> The C-SiC thermocouple is coming into wider use, particularly in the measurement of steel temperatures.<sup>7</sup> It has the advantages of high e.m.f. and a long temperature range, and the disadvantage of high resistance.

### Thermopiles

To detect very small changes in temperature, several thermocouples may be arranged in series to form a thermopile. Used with a sensitive galvanometer, this provides a highly sensitive detector for radiation in spectroscopic investigations, etc.

Fine silver and bismuth wires have been used extensively for thermopiles because of their large thermal e.m.f. The construction of such thermopiles requires considerable skill. Recently Launer<sup>8</sup> has described a simplified technique for constructing thermopiles using chromel and constantan wires (of No. 36 and 38 gauge, respectively) with the measuring junctions soldered to silver foil receivers (Fig. 24). The thermoelectric power of such a thermopile is more than 60 mv. per degree C.

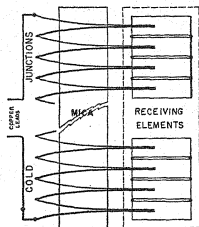


FIG. 24.—Thermopile.

<sup>6</sup> G. Keinath, *Arch. tech. Messen*, 4, 55 (1935).

<sup>7</sup> G. R. Fitterer, *Iron Age*, 140, No. 4, 38 (1937).

<sup>8</sup> H. F. Launer, *Rev. Sci. Instruments*, 11, 98 (1940).

TABLE I  
THERMOCOUPLE CHARACTERISTICS\*

Type.....	Copper-Constantan		Iron-Constantan	
Composition, %.....	100 Cu 99.9Cu	54Cu 46Ni (1) 55Cu 45Ni (10,7)	~ 100Fe (4) 99.9 Fe (10)	55Cu 44Ni .5 Mn + Fe, Si (4) 55Cu 45Ni (10) 60Cu 40Ni (3)
Range of application, °C.	-150 to +320 (1) 0 to 360 (7) -200 to +260 (9)		-200 to +1050 (1,3) 0 to 750 (4)	
Resistivity, $\mu\text{ohm-per}$ cm. cube.	1.73 (7,10) 48.80 (5) 1.71 (9) 49 (7,9,10) 1.751 (5)		10 (4,9,10), 10.13 (5) 49 (4,9,10) 48.8 (5)	
Temperature coefficient of resistivity, $\text{deg.}^{-1}$ C.	.0039 (9) .00002 (9) .00393 (7,10) .0000144 (5) .0040 (5) .00002 (7,10)		.005 (4,9,10) .00002 (9) .0062 (5) .0000144 (5) .00002 (4,10)	
Melting temperature...	1081 (9), 1085 (5), 1190 (9), 1290 (5), 1200 (7)		1530 (10), 1535 (9,4) 1190 (9,10) 1210 (4) ~ 1575 (5) 1250 (8) ~ 1290 (5)	
Maximum temperature: Continuous use, °C...	200 (5), 350 (7,10) 500 (1:21)		500 (1:21), 650 (4), 760 (10), 900 (3)	
Intermittent use, °C.	200 (5), 400 (10), 600 (1:21), 800 (7)		600 (1:21) 760 (4), 1000 (10), 1050 (3)	
E.m.f.: various temps., °C. in mv. (ref. jct. at 0°C.).	100 4.28 mv. (9) 200 9.29 300 14.86		100°C. 5.28 mv. (9) 200 10.78 400 21.82 600 33.16 800 45.48 1000 58.16	
Maximum deviation from manufacturer's calibration.	$\pm 2^\circ\text{C. (10)} \pm 5^\circ\text{C. (5)}$ $0.5^\circ\text{C. at } 150^\circ\text{C. (7)}$ Standard (9): { -300 to +200°F. $\pm 1.5^\circ\text{F.}$ { 200 to 600°F. $\pm 3\frac{1}{4}\%$ Special (9): { -300 to +200°F. $\pm 3\frac{1}{4}\%$ { 200 to 600°F. $\pm 3\frac{1}{4}\%$		$\pm 2^\circ\text{C. (10), } \pm 3^\circ \text{ to } 550^\circ, \pm 1\frac{1}{2}\% \text{ above}$ $550^\circ (4), \pm 5^\circ \text{ at } 900^\circ (5)$ Standard (9): { 32 to 500°F. $\pm 5^\circ\text{F.}$ { 500 to 1650°F. $\pm 1\%$ Special (9): { 32 to 500°F. $\pm 2^\circ\text{F.}$ { 500 to 1000°F. $\pm 1\frac{1}{2}\%$ { 1000 to 1500°F. $\pm 1\frac{1}{4}\%$	
Influence of tempera- ture and gas atmos- phere.	Subject to oxidation and altera- tion above 400° due Cu, above 600° due constantan wire. Ni-plating of Cu tube gives protection in acid-con- taining gas. Contamination of Cu affects calibration greatly (1). Resistance to oxid. atm.: good (5). Resis- tance to reducing atm.: good (5,9). Requires protection from acid fumes (5).		Oxidizing and reducing atm. have little effect on accuracy. Best used in dry atm. (1). Resistance to oxidation: good up to 400°C. (9,10), but poor above 700°C. (9). Resistance to reducing atm.: good (4,5,9); good to 400°C. (10). Protect from oxygen, moisture (5); sulphur (4,9).	
Particular applications.	Low temperature (1,9). Industrial (9,10). Internal combustion engine (10). Used as a tube element for measurements in steam line (1).		Industrial applications up to 800°C., particu- larly for reducing atmospheres (9,9,10). Steel annealing, boiler flues, tube stills (4). Used in reducing or neutral atm. (4)	

\*For footnote see page 71.

TABLE I.—(Continued)

Type.....	Chromel-Constantan
Composition, %.....	90Ni 10Cr (8,1:21), 55Cu 45Ni (7,1:21)
Range of application, °C.....	0 to 1100 (7), 300 to 1000 (1)
Resistivity, $\mu$ ohm-per cm. cube.....	70 (7), 87 (1:21) 49 (7), 52 (1:22) 100 (1:21; 1:24), 110 (1:23) 50 (1:21; 1:24)
Temperature coefficient of resistivity, $\text{deg.}^{-1}$ C.....	.000349 (8) .0002 (8) .00004 (1:21) .00005 (1:21) .00020 (1:22, 1:23) .00016 (1:22; 1:23)
Melting temperature.....	1400 (1:21), 1410 (1:24), 1100 (1:21), 1200 (7) 1420 (1:22), 1370 (1:23), 1250 (1:23), 1350 (1:22)
Maximum temperature: Continuous use, °C.....	800 (8), 500 (1:21), 600 (1:22; 1:23)
Intermittent use, °C.....	1100 (8), 600 (1:21), 800 (1:23), 900 (1:22)
E.m.f.: various temps., °C. in mv. (ref. jet. at 0°C.).	100° 6.3 mv. (7) 200 13.3 400 28.5 600 44.3
Maximum deviation from manufacturer's calibration	3° at 500°C. (7)
Influence of temperature and gas atmosphere.....	Chromel attacked by sulphurous atm. (1). Resistance to oxidation good (7). Resistance to reducing atm. poor (7).
Particular applications.....	

## Protection tubes

Closed-end tubes of porcelain, of pyrex glass or of materials listed in Table II are generally used to protect thermocouples from contamination, which usually results from the thermocouple wires coming in contact with other metals or metallic vapors or from the action of reducing gases at high temperatures. In the latter case, the silica of the insulating or protecting tube is reduced to silicon which alloys with the thermocouple wires. For temperatures above 600°C. the wires should be insulated by porcelain tubing and protected from contamination by a glazed porcelain tube. For temperatures below 600°C., pyrex tubes are very satisfactory for both protecting and insulating the wires. An additional sheath of metal, alundum or quartz is used when mechanical strength is required, as in measurements in molten metals.

Tests on the permeability of various protection tubes to gas leakage have shown very refractory porcelain, mullite or

TABLE I.—(Continued)

Type.....	Chromel-Alumel		Carbon-Silicon carbide (tube element)	
Composition, %.....	90Ni 10Cr (8.1:23) 89-6Ni 8-9Cr (3) 89Ni 10Cr (1:22) 89Ni 9.8Cr 1Fe 0.2- Mn (1:25)	95Ni 2Al 2Mn 1Si (8) 97Ni 3Al + Si (4) 94Ni 2Al 1Si 2.5Mn 0.5Fe (1:25)	C	SiC
Range of application, °C.....	0 to 1100 (4), 0 to 1250 (3), 500 to 1250 (1)		to 2000°C. (6)	
Resistivity, $\mu$ ohm-per cm. cube.....	70.5 (5), 69.4 (8), 29.4 (5), 28.6 (8), 30 (4)			
Temperature coefficient of resistivity, deg. °C.	.00032 (4) .00014 (4) .000324 (5) .000144 (5) .000349 (8) .000225 (8)			
Melting temperature.....	1400 (4), 1430 (5) 1450 (3)	1400 (4), 1430 (5) 1450 (3)	3000° (6) 2700° ? (6)	
Maximum temperature: Continuous use, °C.....	1100 (3,4), 1200 (5), 1260 (8)			
Intermittent use, °C.....	1200 (4), 1250 (3), 1320 (8), 1370 (5)			
E.m.f.: various temps., °C. in mv. (ref. jct. at 0°C.)	100°C. 4.1 mv. (8) 200 8.13 400 16.39 600 24.90 800 33.31 1000 41.31 1200 48.85 1400 55.81		1210° 353.6 mv. (6) 1300 385.2 1360 403.2 1450 424.9	
Maximum deviation from manufacturer's calibration.	{ 0 to 349°C. $\pm$ 3°C. } (4) { 349 to 1260° $\pm$ 3½% } (4) { 32 to 660°F. $\pm$ 5°F. } (5), 3½% (8) { Above 660°F. $\pm$ 3½% } (5), 3½% (8) Standard (9): { 0 to 660°F. $\pm$ 5°F. 660 to 2300°F. $\pm$ 3½% } Special (9): { 0 to 660°F. $\pm$ 3°F. 660 to 2300°F. $\pm$ 3½% }		1%?	
Influence of temperature and gas atmosphere.	Resistance to oxidizing atm.: good (3,4), very good (5,8,9). Resistance to reducing atm.: poor (3,4,5,8,9). Affected by sulphur (4), reducing or sulphurous gas (8), SO <sub>2</sub> and H <sub>2</sub> S(5).		Used as tube element. Carbon sheath chem- ically inert (6).	
Particular applications.....	Used in oxidizing atm. (4). Industrial (9) ceramic kilns, tube stills, electric furnaces (4).		Steel furnace and ladle temperatures (10). Laboratory meas.	

sillimanite to be especially suitable.<sup>9</sup> Calorized wrought iron is superior to most other metals. Nichrome is generally more gas tight than other alloys. Gas often enters the tubes through tiny pin-hole imperfections rather than by diffusion through the walls. Ceramic tubes become less permeable to gas at higher temperature, possibly owing to increased gas viscosity.<sup>10</sup>

<sup>9</sup> W. F. Roeser, *Nat. Bur. Standards J. Research*, 7, 485 (1931).

<sup>10</sup> W. Miehr, *Ber. deut. keram. Ges.*, 12, 29 (1932).

TABLE I.—(Continued)

Type.....	Pt-PtRh [10]		Pt-PtRh [13]	
Composition, %.....	Pt 0 to 1500 (4)	90Pt 10Rh	Pt	87Pt 13Rh
Range of application, °C. ....	0 to 1550 (3)	800 to 1600 (1)		
Resistivity, $\mu\text{ohm-per cm. cube.}$	10 (9, 1:21, 1:24) 11 (4, 1:22, 1:23)	19 (4) 20 (1:21, 1:22, 1:24) 21 (9, 1:23) 24.8 (2)		
Temperature coefficient of resistivity, $\text{deg.}^{-1} \text{ C.}$	.0030 (4,9) .0039 (1,2)	.0013 (2, 1:21) .0018 (2,4) .0020 (1:23), .0024 (1:22)		
Melting temperature.....	1773 (2,4,9),	1700 (3), 1793 (4) 1800 (2)		
Maximum temperature: Continuous use, °C. ....	1300-1400 (2), 1450 (3), 1500 (4,1)			
Intermittent use, °C. ....	1500 (2), 1550 (3), 1650 (4,1)			
E.m.f.: various temps., °C. in mv. (ref. jet. at 0°C.).	100° 0.643 mv. (9) 200 1.436 400 3.251 600 5.222 800 7.330 1000 9.569 1200 11.924 1400 14.312 1600 16.674		100° 6.46 mv. (9) 200 1.464 400 3.398 600 5.561 800 7.927 1000 10.470 1200 13.181 1400 15.940 1600 18.680	
Maximum deviation from manufacturer's calibration.	$\pm 5^\circ$ (4) Standard to 2000°F. $\pm \frac{1}{2}\%$ (9) Special to 2000°F. $\pm \frac{1}{4}\%$ (9) $\pm 3^\circ$ at 1200°C. (2)			
Influence of temperature and gas atmosphere.	Resistance to oxidizing atm. very good (4,5-8,9). Resistance to reducing atm. poor (4,5,8,9). Susceptible to chemical alteration by As, Si, P vapor in reducing gas ( $\text{CO}_2$ , $\text{H}_2$ , $\text{H}_2\text{S}$ , $\text{SO}_2$ ) (1,4,5). Pt corrodes easily above 1000°. Used in gas-tight protecting tube.			
Particular applications.....	International standard 630 to 1063°		Similar to Pt-90Pt 10Rh, but has higher e.m.f.	

\* Parentheses following the data in Table I indicate the source of the information as follows:

(1) H. Euler and K. Guthmann, *Arch. Eisenhüttenw.* 9 No. 2 73 (1935).

(2) Baker & Co.

(3) The Bristol Co.

(4) The Brown Instrument Co.

(5) Charles Engellhard, Inc.

(6) Fitterer Pyrometer Co.

(7) General Electric Co.

(8) Hoskins Manufacturing Co.

(9) Leeds and Northrup Co.

(10) Lewis Engineering Co.

(1:21) H. Euler and K. Guthmann . .  
W. C. Heraeus, GmbH, Hanau.

(1:22) — G. Siebert, GmbH, Hanau.

(1:23) — Hartmann & Braun, Frankfurt a. M.

(1:24) — Siemens & Halske, Berlin-Siemensstadt.

When a thermocouple is used for measurements in molten metal at high temperatures, it is customary to increase the thickness of the protection tube. This has certain disadvantages: the long time required for pre-heating to avoid fracture of the sheath, and for attaining equilibrium on immersion; the risk of damage to the sheath in the bath; and the danger of contamination of the couple by reducing gases.

An alternative "quick-immersion" technique has been developed<sup>11</sup> enabling the Pt-PtRh<sub>6</sub> thermocouple to be used for regular measurements in liquid steel up to 1700°C. It consists essentially in lightly sheathing the couple in silica thus allowing its sudden immersion in the steel, the taking of readings in a few seconds, and the withdrawal of the thermocouple intact. The arrangement of the end of the apparatus to be immersed in steel is shown in Fig. 25. To reduce the lag, one may dispense with the steel jacket *B* and the lower portion of the two-bore insulator *C*. The time necessary to get a temperature reading ranges from 4 to 15 seconds according to circumstances. If necessary the short inexpensive silica sheath is replaced after each insertion. The thermocouple will stand from 10 to 20 immersions without appreciable contamination, and the full e.m.f. can readily be restored by cutting off an inch or two from the heated end.

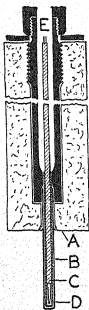


FIG. 25.—  
Quick-immersion thermocouple.

### Thermocouple calibration at fixed points

A thermocouple is calibrated by measurement of its e.m.f. at fixed points whose temperatures are assigned, or by comparison with a previously-calibrated couple placed in good thermal contact with it.

<sup>11</sup> F. H. Schofield and A. Grace, *Iron and Steel Inst. (London) Special Report 25*, section VII, 235 (1939).

TABLE II  
 THERMOCOUPLE PROTECTION TUBE MATERIALS

Material	Maximum temperature	Composition, characteristics and applications
Copper.....	500°C.	Cu 90Cu, 10Sn } Copper is nickel- or chromium-plated against oxidation.
Bronze.....	.....	
Monel.....	.....	67-70Ni, 30Cu } Low temperature steam.
Seamless steel.....	550	Used in hydrogen, ammonia or any atm. not corrosive.
Wrought iron.....	700	Boiler flues, ammonia, hydrogen atm. Scales rapidly at high temp. in presence of oxygen.
Cast iron.....	700	Generally more useful than wrought iron in chemical industry. Resistant to sulphuric and caustic solutions.
Calorized wrought iron.	800	Iron coated with mixture of Al-Al <sub>2</sub> O <sub>3</sub> . More resistant to corrosion than wrought iron. Used in pipe-type couples, boiler flues.
Stainless steel.....	800	0.05-.20C, 18Cr, 8Ni rem. Fe. High oxidation resistance. Attacked by sulphur. Used in tube stills.
14% Chrome iron.....	800	Resistant to chemical corrosion, particularly sulphur.
18% Chrome 8% nickel iron.	800	Resists corrosion. Protection wells in steam or wet processes. Steam temperatures.
28% Chrome iron.....	1100	General purpose alloy. More resistant to corrosion than 14% chrome iron. Used in neut., red., or ox. atm., for carburizing, etc.



TABLE II.—(Continued)

Material	Maximum temperature	Composition, characteristics and applications
32% Nickel 20% chrome iron.	1100°C.	Good mechanical strength, and resistance to sulphur (more than higher nickel alloys, less than 28% chrome iron). General high temp. use except in sulphurous atm.
Nichrome.....	1100	Good creep strength. High resistance to oxidation. Attacked by sulphur. Electric furnaces.
Nichrome.....	1100	38Ni, 18Cr . . . Resists sulphur fumes.
Nichrome.....	1150	67Ni, 20Cr . . . For general heat treating where high mechanical strength desired.
Chromel S (cast).....	1100	For gases containing sulphur.
Chromel T (cast).....	1100	For oxidizing or reducing gases, sulphur-free.
D Nickel.....	900	94.75Ni + Co, .1C, .1Si, .2Fe, .008S, .07Cu, 4.75Mn To 900C in sulphur-free atm. To 300–500 in sulphurous, ox. atm.
A Nickel.....	1050	99.40Ni + Co, .1C, .05Si, .005S, .1Cu, .15Fe, .2Mn To 1050 in sulphur-free atm. To 300–550 in sulphurous ox. atm. To 250–400 in sulphurous red. atm. Should not be used where sulphur content exceeds .5%.
Iconel.....	1100	78Ni + Co, .08C, .3Si, .012S, .4Cu, 8Fe, .6Mn, 13.5Cr. To 1100 in sulphur-free atm. To 800 in sulphurous, ox. atm. To 550 in sulphurous, red. atm. Superior to A, D nickel, for carburizing, brazing, nitriding, etc. Should not be used where sulphur content exceeds .5%.

TABLE II.—(Continued)

Material	Maximum temperature	Composition, characteristics and applications
Fused quartz.... .	1000–1400°C.	99.8–100SiO <sub>2</sub> . Rapid reaction with basis fluxes. Slow reaction with acid fluxes. Good resistance to ox. atm. Affected by red. atm. at high temp. Excellent resistance to spalling.
Porcelain.....	1300	71SiO <sub>2</sub> , 21Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> and other oxides. Rapid reaction with basic fluxes. Slow reaction with acid fluxes except at high temp. Not affected by red. atm. Good resistance to spalling.
Fire clay.....	1400	53SiO <sub>2</sub> , 43Al <sub>2</sub> O <sub>3</sub> , 2.3Fe <sub>2</sub> O <sub>3</sub> and other oxides. Rapid reaction with basic fluxes. Slow reaction with acid fluxes except at high temp. Good resistance to ox. atm. Not affected by red. atm. Good spalling resistance.
Mullite base refractory..	1300 horiz. 1500 vert.	Not impervious to gas. Primary and secondary protection for rare-metal couples.
Silica.....	1500	Rapid reaction with basic fluxes. Slow reaction with acid fluxes. Good resistance to ox. atm. Affected by red. atm. at high temp. Poor spalling resistance.
Sillimanite.....	1600–1800	37SiO <sub>2</sub> , 63Al <sub>2</sub> O <sub>3</sub> . Rapid reaction with basic fluxes. Slow reaction with acid fluxes. Good resistance to ox. atm. Not affected by red. atm. Good spalling resistance. Used in ceramic kilns, as a secondary protection tube, and where resistance to cutting action of flames and gases is necessary.

TABLE II.—(Continued)

Material	Maximum temperature	Composition, characteristics and applications
Mullite.....	1650°C.	28SiO <sub>2</sub> , 72Al <sub>2</sub> O <sub>3</sub> , (3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ). Rapid reaction with basis fluxes. Fairly slow reaction with acid fluxes. Good resistance to ox. atm. Not affected by red. atm. Good spalling resistance.
Silicon carbide.....	1650	SiC. Softens about 1750°C., decomposes at higher temp. Fairly rapid reaction with basic fluxes. Slow reaction with acid fluxes. Fair resistance to oxidation above red heat. Not affected by red. atm. Excellent spalling resistance.
ThO <sub>2</sub> , BeO, ZrO <sub>2</sub> .....	2000	Excellent refractories. Expense limits use.

Calibration of a thermocouple at a few selected fixed points will yield a working standard which is accurate to a few tenths of a degree in the range 0° to 1100°C. Fixed points are also conveniently used with varying degrees of accuracy ranging from 0.1° to 5°C. in the calibration and checking of various types of thermocouples in the range -190°C. to the melting point of platinum (1773°C.). The fixed points for which values have been assigned or determined accurately and at which it has been found convenient to calibrate thermocouples are given in Table III.<sup>12</sup> (Page 85.)

The e.m.f. developed by a homogeneous thermocouple at the freezing point of a metal is constant and reproducible if all of the following conditions are fulfilled: (1) the couple is protected from contamination; (2) the couple is immersed in the freezing-point sample sufficiently to eliminate heating or

<sup>12</sup> W. F. Roeser and H. T. Wensel, *J. Research Nat. Bur. Standards*, 14, 274 (1935).

cooling of the junction by heat flow along the wires and protection tube; (3) the reference junctions are maintained at a constant and reproducible temperature; (4) the freezing-point sample is pure; and (5) the metal is maintained at essentially a uniform temperature during freezing.

The temperature of the reference junctions is most easily controlled at a known temperature by placing them in an ice bath. A widemouthed thermos bottle filled with shaved ice saturated with water is very satisfactory. Electrical connection between a thermocouple wire and a copper lead wire is easily made by inserting them into a small glass tube containing a few drops of mercury. The glass tubes are then inserted into the ice bath to a depth of about 10 cm. The lead wires should be insulated from the thermocouple wires, except where they make contact through the mercury. The glass tubes should be kept clean and dry inside. Moisture is likely to condense in the tube from the atmosphere but should not be allowed to accumulate. A little moisture and dirt at the bottom of the tube will form a galvanic cell which may vitiate the readings.

The depth of the immersion necessary to avoid heating or cooling of the junction by heat flow along the thermocouple wires and protection tube depends upon the material and size of the wires, the dimensions of the insulating and protecting tubes, and the difference between the temperature of the freezing-point sample and that of the furnace and atmosphere immediately above it. The safest method of determining whether the depth of immersion is sufficient is by trial. It should be such that during the period of freezing the thermocouple can be lowered or raised at least 1 cm from its normal position without altering the indicated emf by as much as the allowable uncertainty in the calibration.

Figure 26 shows the type of furnace used in freezing point determinations. The heating element is no. 6 or 8 gauge 80Ni20Cr wire wound on an alundum tube and imbedded in alundum cement. The space between the heating element

and the outside wall is filled with silocel powder. Acheson-graphite diaphragms are placed above the crucible in order

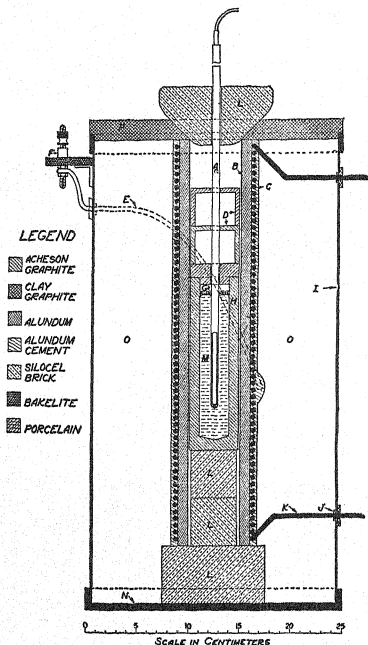


FIG. 26.—Furnace used in calibrating thermocouples at freezing points of metals.

to minimize the oxidation of the crucible and to promote temperature uniformity in the metal.

Calibrations at the steam point are made by the use of a hypsometer constructed to avoid superheating the vapor

around the thermocouple and contamination with air and other impurities.<sup>13</sup> A simple type of hypsometer suitable for calibrations not requiring the highest accuracy is illustrated in Fig. 27.

### Thermocouple calibration by comparison method

The calibration of a thermocouple by comparison with a working standard is sufficiently accurate for most purposes and can be done conveniently in most industrial and technical laboratories. The success of this method usually depends upon the ability of the observer to bring the junction of the couple to the same temperature as the actuating element of the standard, such as the hot junction of a standard thermocouple or the bulb of a resistance or liquid-in-glass thermometer. The accuracy obtained is further limited by the accuracy of the standard. Of course, the reference-junction temperature must be known, but this can usually be controlled by using an ice bath as described earlier or measured by a liquid-in-glass thermometer. The method of bringing the junction of the couple to the same temperature as that of the actuating element of the standard depends upon the type of couple, type of standard, and the method of heating.

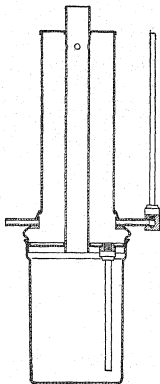


FIG. 27.—Hypsometer.  
(Central Scientific Co.)

In order to insure equality of temperature between the measuring junction of the couples in the furnace, they may be inserted in holes drilled in a copper or nickel block, or they may be welded together as in Fig. 28. Separate potentiometers, one connected to each couple, are used to measure the

<sup>13</sup> E. F. Mueller and T. S. Sligh, Jr., *Rev. Sci. Instruments*, 6, 958 (1922).

e.m.f.'s. To permit simultaneous readings, each potentiometer is provided with a reflecting galvanometer. The two spots of light are reflected on a single scale, the galvanometers being set so the spots coincide at zero on the scale when the circuits are open, and hence also when the potentiometers are set to balance the e.m.f. of each couple. One potentiometer is set to a determined value and the other adjusted so both spots of light pass across the zero of the scale together as the temperature of the furnace is raised or lowered. This method is particularly adapted to the calibration of thermocouples at any number of selected points.

### Methods of interpolating between calibration points<sup>14</sup>

After the thermocouple has been calibrated at a number of points, the next requirement is a convenient means of obtain-

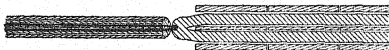


FIG. 28.—Arrangement to insure good thermal contact between junction of a base-metal thermocouple and that of a Pt-PtRh couple.

ing corresponding values of e.m.f. and temperature at other points. A curve may be drawn or a table giving corresponding temperature and e.m.f. values may be prepared. The values in such a table may be obtained by computing an empirical equation or series of equations through the calibration points, by direct interpolation between points, or by drawing a difference curve from an arbitrary reference table which closely approximates the temperature-e.m.f. relation of the couple. The method to be selected for a particular calibration depends upon such factors as the type of couple, number of calibration points, temperature range, accuracy required, and personal preference.

For the highest accuracy in the range 660° to 1063°C. with platinum to platinum-10 per cent rhodium thermo-

<sup>14</sup> W. F. Roeser, *Bur. Standards J. Research*, 3, 343 (1929).

couples, the method is that prescribed in the International Temperature Scale. An equation of the form  $e = a + bt + ct^2$ , where  $a$ ,  $b$ , and  $c$  are constants determined by calibration at the freezing points of gold, silver, and antimony, is used. By calibrating the couple also at the freezing point of zinc and using an equation of the form  $e = a' + b't + c't^2 + d't^3$ , the temperature range can be extended down to  $400^\circ\text{C}$ . without introducing an uncertainty of more than  $0.1^\circ\text{C}$ . in the range  $660^\circ$  to  $1063^\circ\text{C}$ . By calibrating the couple at the freezing points of gold, antimony, and zinc and using an equation of the form  $e = a'' + b''t + c''t^2$ , a calibration is obtained for the range  $400^\circ$  to  $1100^\circ\text{C}$ ., which agrees with the International Temperature Scale to  $0.5^\circ\text{C}$ . The freezing point of copper may be used instead of the gold point, and the aluminum point used instead of the antimony point without introducing an additional uncertainty of more than  $0.1^\circ\text{C}$ .

For temperatures outside the range  $660^\circ$  to  $1063^\circ\text{C}$ ., the method of drawing a smooth curve through the temperature and e.m.f. values has just as much claim to accuracy as the method of passing empirical equations through the calibration points, because an empirical equation performs the same function as a curved ruler. For the temperature range 0 to  $1500^\circ\text{C}$ ., a curve for interpolation to  $1^\circ$  or  $2^\circ\text{C}$ . requires calibration points not more than  $200^\circ\text{C}$ . apart and a careful plot on a large sheet of paper, which is tedious to read. A reduction in the number of calibration points increases the uncertainty proportionately. If, however, we plot as ordinates the differences between the observed e.m.f. and that calculated from the first degree equation  $e = 10t$ , and e.m.f. as abscissas, the difference at intermediate points may be taken from the curve and added to the quantity  $10t$  to obtain values of e.m.f. corresponding to the appropriate temperature in which the uncertainty in the interpolated values is much less than in the case in which the e.m.f. is plotted directly against the temperature. If we go one step further and plot



differences from an arbitrary reference table the values of which closely represent the form of the temperature-e.m.f. relation for the type of couple in question, the maximum differences to be plotted will be only a few degrees. In this way interpolated values are obtained in which the uncertainty in the interpolated values is not appreciably greater than that at the calibration points. The more accurately the values in the arbitrary reference table conform to the e.m.f.-temperature relation of actual couples, the fewer the number of calibration points required for a given accuracy.

The materials used in the construction of base-metal thermocouples generally are not as pure as those used for rare-metal thermocouples, nor is this necessary. Manufacturers have adopted somewhat different calibration curves for thermocouples having the same name but differing slightly in thermoelectric properties. Replacement couples having the same calibration are provided by controlling the composition of the elements, or by selecting pairs of materials from different heats which will match the predetermined calibration. This also leads, for example, to the occasional use of a different composition of constantan for iron-constantan and for copper-constantan thermocouples.

Specifications for iron-constantan and copper constantan thermocouples have recently been established<sup>15</sup> in an attempt to meet the first two essential requirements and the last three desirable conditions listed below:

(1) The calibration should be such that it can be reproduced over a large temperature range with materials readily available at present (and presumably in the future).

(2) It should be the same (within reasonable limits) as the temperature-e.m.f. relation of a large percentage of such thermocouples now in use.

(3) It should be near the mean of the extreme limits of the temperature-e.m.f. relation for thermocouples of that type.

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<sup>15</sup> W. F. Roeser and A. I. Dahl, *J. Research Nat. Bur. Standards*, **20**, 337 (1938).

(4) It should agree with the most widely used existing table.

(5) The constantan selected for use with copper to reproduce the relation for copper-constantan should be such that it can be used with a particular iron to reproduce the relation for iron-constantan as well. Typical tables are given in the Appendix.

### Reference junction corrections

It is not always possible to maintain the reference junctions (commonly called cold junctions) at a desired temperature during the calibration of a thermocouple, but if the temperature of the reference junctions is measured it is possible to apply corrections to the observed e.m.f. which will yield a calibration with the desired reference-junction temperature. If the e.m.f. of the couple is measured with the reference junctions at temperature  $t$ , and a calibration is desired with these junctions at temperature  $t_0$ , the measured e.m.f. may be corrected for a reference-junction temperature of  $t_0$  by adding to the observed value the e.m.f. which the couple would give if the reference junctions were at  $t_0$  and the measuring junction at  $t$ . For example, suppose the observed e.m.f. of a platinum-10 per cent rhodium thermocouple with the measuring junction at  $1000^{\circ}\text{C}$ . and the reference junction at  $25^{\circ}\text{C}$ . is 9.43 mv., and the e.m.f. of the couple with the measuring junction at  $1000^{\circ}\text{C}$ . and the reference junctions at  $0^{\circ}\text{C}$ . is required. The e.m.f. of the couple when the reference junctions are at  $0^{\circ}\text{C}$ . and the measuring junction at  $25^{\circ}\text{C}$ . is 0.14 mv. The sum of these e.m.f.'s (9.43 and 0.14) gives the desired value.

The sign of the corrections must be considered when applying these corrections,

If the thermocouple is very short, so that the reference junctions are near the furnace and subject to considerable variations or uncertainty in temperature, it is usually more convenient to use extension leads to transfer the reference

junctions to a region of more constant temperature than to measure the temperature of the reference junctions near the furnace. The extension leads of base-metal couples are usually made of the same materials as the thermocouple wires, but in the case of platinum-rhodium couples a copper lead is connected to the platinum-rhodium wire and a copper-nickel lead to the platinum wire.

### Thermocouple indicators

Instruments for the measurement of e.m.f.'s generated by thermocouples fall into four classes: (i) galvanometers or millivoltmeters, (ii) potentiometers, (iii) deflection potentiometers, which combine features of the first two, and (iv) electron tube potentiometers.

A millivoltmeter is essentially a d'Arsonval galvanometer, having a moving coil mounted between the poles of a permanent magnet. An e.m.f. applied to the terminals of the instrument causes the current-carrying coil to be deflected in the magnetic field until the electromagnetic torque is balanced by the mechanical torque of a small control spring. The coil is supported either on two pivots at the ends of its shaft, or on a single pivot at its center of gravity.

In the laboratory use of thermocouples, the reference junction is usually kept in melting ice. This may not be practical in industrial use, hence methods of compensating for variation in reference junction temperature have been devised. One method uses a small bi-metallic strip to vary the tension on the control spring in the millivoltmeter as the reference temperature (i.e., room temperature) varies. Another uses automatic electrical reference junction compensation in the form of a Wheatstone network one arm of which is a coil of wire having a high temperature coefficient of resistivity.

An objection to the use of millivoltmeters is that they indicate an e.m.f. less than the value developed by the thermocouple. A (small) current is required to actuate

the indicator. This results in a fall in potential in the line and couple equal to the product of their resistance times the current.

TABLE III  
FIXED POINTS AVAILABLE FOR CALIBRATING THERMOCOUPLES

Thermometric fixed point	Values on the International Temperature Scale				Temperature of equilibrium ( $t_p$ ) in °C. as a function of the pressure ( $p$ ) between 680 and 780 mm. of Hg
	Assigned (Primary points)		Determined (Secondary points)		
	°C.	°F.	°C.	°F.	
Boiling point of oxygen....	-182.97	-297.35			$t_p = t_{760} + 0.0126(p - 760) - 0.000065(p - 760)^2$
Sublimation point of carbon dioxide. }			-78.5	-109.3	$t_p = t_{760} + 0.1443(t_p + 273.2) \log \left( \frac{p}{760} \right)$
Freezing point of mercury..			-38.37	-37.97	
Melting point of ice.....	0.000	32.000			
Boiling point of water.....	100.000	212.000			$t_p = t_{760} + 0.0367(p - 760) - 0.000023(p + 760)^2$
Boiling point of naphthalene			217.96	424.33	$t_p = t_{760} + 0.208(t_p + 273.2) \log \left( \frac{p}{760} \right)$
Freezing point of tin <sup>1</sup> .....			231.9	449.4	
Boiling point of benzophenone.			305.9	582.6	$t_p = t_{760} + 0.194(t_p + 273.2) \log \left( \frac{p}{760} \right)$
Freezing point of cadmium.....			320.9	609.6	
Freezing point of lead <sup>1</sup> .....			327.3 <sub>5</sub>	621.2 <sub>3</sub>	
Freezing point of zinc <sup>1</sup> .....			419.4 <sub>2</sub>	787.0 <sub>6</sub>	
Boiling point of sulphur...	444.60	832.28			$t_p = t_{760} + 0.0909(p - 760) - 0.000048(p - 760)^2$
Freezing point of antimony.....			630.5	1166.9	
Freezing point of aluminum <sup>1</sup> .....			660.1 <sub>3</sub>	1200.2 <sub>7</sub>	
Freezing point of Cu-Ag eutectic alloy. <sup>2</sup> .....			778.8	1433.8	
Freezing point of silver.....	960.5	1760.9			
Freezing point of gold.....	1063.0	1945.4			
Freezing point of copper <sup>1</sup> ..			1083.0	1981.4	
Melting point of palladium.....			1555	2831	
Melting point of platinum..			1773	3223	

<sup>1</sup> Standard samples of these materials are procurable from the National Bureau of Standards with certificates giving the freezing point of the particular lot of metal. The values given in this table for these materials apply for the standard samples that are being issued as of the present date.

<sup>2</sup> 28.1 per cent copper and 71.9 per cent silver by weight.

The scale of the millivoltmeter can be calibrated arbitrarily to read the correct e.m.f. for a fixed line and couple

resistance. If the resistance varies, however, error is introduced. These difficulties are minimized if the millivoltmeter has a high resistance.

Consider a millivoltmeter calibrated to read the potential difference across its terminals,  $e_v$ . Let  $e$  represent the true e.m.f. of the couple,  $R_v$  the resistance of the millivoltmeter,  $R_c$  the resistance of the line and couple. Then from Ohm's law:

$$e_v = \frac{R_v}{R_c + R_v} e \quad (1)$$

It is evident that if  $R_v$  is large compared to  $R_c$ , the ratio  $R_v/(R_c + R_v)$  becomes nearly unity and  $e_v$  differs but little from  $e$ . A high-resistance millivoltmeter is affected less by change in line resistance than is a low-resistance instrument. Assume that a 300-ohm and a 10-ohm millivoltmeter have been calibrated for an external resistance of 2 ohms. Table

TABLE IV  
ERROR DUE TO CHANGE IN LINE RESISTANCE

Line resistance (ohms)	Error in indicator reading		Error in degrees at 1000°C.	
	300 ohms	10 ohms	300 ohms	10 ohms
	per cent	per cent	°C.	°C.
1	+0.33	+ 9.1	+3.3	+ 91.0
2	±0.00	± 0.0	±0.0	± 0.0
3	-0.33	- 7.7	-3.3	- 77.0
4	-0.66	-14.3	-6.6	-143.0

IV shows the errors which will occur in the readings (using a certain base-metal couple) if the external resistance changes to 1, 3 or 4 ohms. Variation in line resistance may be caused by oxidation of the wires, poor contacts, temperature variations in the line and by partial fracture of the lead wires. If a millivoltmeter, particularly a low-resistance one, is to be used where there is considerable variation in line resistance, the meter may be provided with a variable resistance in series with its moving coil. It is initially calibrated with

this resistance at its maximum. In service this resistance is repeatedly adjusted to compensate for changing (increasing) line resistance.

Precision laboratory measurements of thermocouple e.m.f.'s as well as most industrial plant thermocouple measurements are made with potentiometers. The potentiometer principle is of such general importance and applicability that it merits careful study. Consider the circuit of Fig. 29 in which a battery  $W$  produces a potential difference between the ends of a uniform resistance wire  $OB$ . A current will

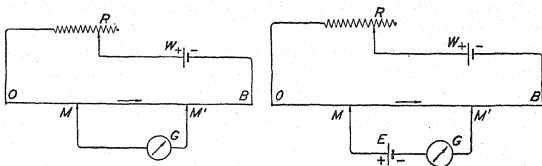


FIG. 29.—Potentiometer principle.

flow in the directions indicated by the arrows, branching at  $M$  to flow in both parts of the divided circuit. A galvanometer  $G$  placed in the lower arm of this circuit will be deflected, indicating a current in that branch. Suppose a cell  $E$  whose e.m.f. opposes and exactly balances the fall in potential provided by  $W$  between points  $M$  and  $M'$  is introduced in the lower branch. There will then be no net current in the lower branch and the galvanometer will be undeflected.

Preparatory to measuring an unknown e.m.f., a standard cell of known e.m.f. is placed at  $E$ . The sliding contacts  $M$  and  $M'$  are adjusted to bring the galvanometer deflection to zero. If  $E_s$  represents the standard cell e.m.f.,  $a_s$  the distance between  $M$  and  $M'$  and  $r$  the resistance per unit length of slide wire, the equation which expresses this balanced condition is

$$E_s = a_s r i \quad (2)$$

The standard cell is then removed and the source of unknown e.m.f.,  $E$ , substituted. A new position of the slide contacts

is found for which the galvanometer deflection is zero. Calling the new distance between  $M$  and  $M''$   $a$ , we have

$$E = ari \quad (3)$$

From the last two equations

$$E = \frac{a}{a_s} E_s \quad (4)$$

Hence if the current  $i$  in  $OB$  can be kept constant, unknown e.m.f.'s can be measured by this method. If  $a_s$  were numerically equal to  $E_s$  the unknown e.m.f. would be numerically equal to the linear distance  $a$  and the instrument would be said to be direct-reading. A potentiometer can be made direct-reading if initially  $a_s$  is made equal to  $E_s$  and balance obtained by adjusting resistance  $R$  rather than the slide contacts  $M$  or  $M'$ . Unfortunately the e.m.f. of the working battery  $W$  will not remain exactly constant, hence frequent standardizations of the potentiometer current by the method just outlined are advisable during prolonged use.

A potentiometer differs from other e.m.f.-measuring instruments in that when the galvanometer shows a balance, no current flows in the circuit of which it is a component. The potentiometer principle represents a null method of measurement. The galvanometer in such service is sometimes called a null-point indicator. Readings are independent of the characteristics of the galvanometer, but depend on the accuracy of the standard cell voltage and the uniformity of the slide wire.

The precision with which the opposing e.m.f.'s can be balanced depends upon the sensitivity of the galvanometer and upon the effective length of the calibrated resistance and its scale. For this reason part of resistance  $OB$  is usually in the form of a slide wire on which contact  $M'$  is continuously adjustable and the remainder in the form of fixed resistances with a dial switch for adjusting  $M$  in uniform steps. This is illustrated in Fig. 31, which is a circuit typical of many port-

able potentiometers. The use of a switch for convenience in interchanging  $E$  and  $E_s$  is also shown.

If the reference junction temperature of the thermocouple differs from  $OC$  a correction must be made in the measured e.m.f. before the standard conversion tables are used to find the temperature of the measuring junction. The ways in which such corrections may be made conveniently on a potentiometer are illustrated by the series of diagrams in Fig. 30.

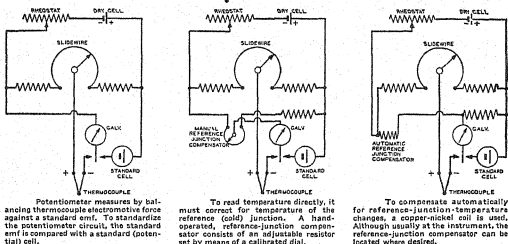


FIG. 30.—Evolution of a potentiometer circuit. (Leeds & Northrup Co.)

## Extension lead wires

To secure the advantages of automatic reference junction compensation, the lead wires used to connect couples to instruments are of the same materials as the couples, or of materials having essentially the same temperature-e.m.f. relationship. A couple is thus in effect extended up to the instrument so that the reference-junction is exposed at the instrument terminal-board to the same ambient temperature as is the compensating coil.

## Precision potentiometer circuits

Figure 31 illustrates the circuit of a portable precision potentiometer. The limit of error of such an instrument is less than 0.1 per cent.



The problem of designing a potentiometer of high precision is largely that of making resistance coils of accurate, permanent calibration and of minimizing the possible errors introduced by parasitic e.m.f.'s in the instrument. It is also desirable to keep the potentiometer resistance in series with the galvanometer substantially constant regardless of the positions of the dial switches.

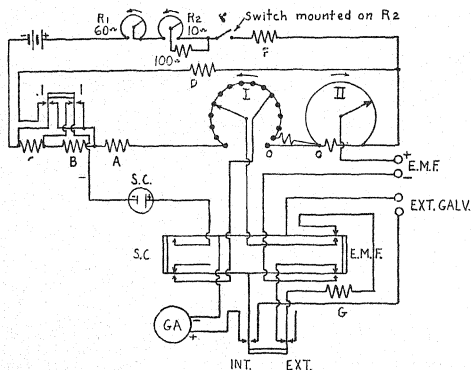


FIG. 31.—Circuit of a portable precision potentiometer. (*The Rubicon Co.*)

As an example of the special circuits<sup>16</sup> that are devised for precision potentiometers, consider Fig. 32 which illustrates the basic principle of the Wenner potentiometer. Two equal resistances  $W$  and  $Y$  are connected in series with  $Z$  and are shunted by the movable resistance  $L$ . The potential between  $P$  and  $Q$  may be varied in known steps by rotating  $L$ . Since  $W$  and  $Y$  are equal, the total resistance between  $N$  and  $P$ , and hence the total current, remain constant. Contact resistances are effectively in the battery circuit rather than

<sup>16</sup> E. F. Mueller and F. Wenner, *J. Research Nat. Bur. Standards*, 15, 477 (1935).

in the circuit  $PQ$  and are in series with  $L$ , so any error due to contact resistance variation is negligible.

Figure 33 shows how this principle is incorporated in the second and third dials of the Wenner thermocouple potentiometer. Measurements with that instrument are made within a limit of error of  $\pm(0.01$  per cent plus 0.5 microvolt) on the high range, or  $\pm(0.01$  per cent + 0.1 microvolt) on the low range. The latter constant factors represent the

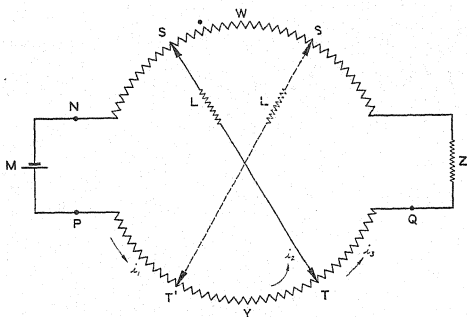


FIG. 32.—Wenner principle. (Leeds & Northrup Co.)

limit of parasitic e.m.f. that even careful design and construction cannot eliminate completely.

Suitable potentiometers are available for measuring thermocouple temperatures to any desired precision. For moderate-precision temperature measurements, a student-type potentiometer (Fig. 158, Exp. 5) is adequate. Figures 34 and 35 represent instruments having accuracies intermediate between smaller portable potentiometers and more precise laboratory instruments, and are used both for laboratory and plant testing. For most on-the-spot checking of plant thermocouples, smaller and, therefore, lighter portable indicators of moderate precision are usually adequate. Because a

single range long enough to accommodate iron-constantan and chromel-alumel couples is only one-quarter utilized by platinum couples, a double range instrument is usually preferred where both base-metal and rare-metal couples are to be checked.

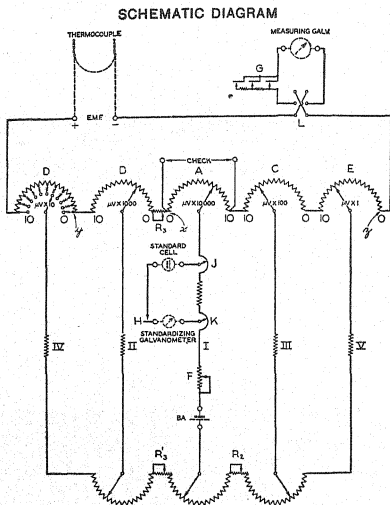


FIG. 33.—Wenner potentiometer circuit. (Leeds & Northrup Co.)

Figure 36 is representative of potentiometers suitable for usual high-precision requirements. Also available for precision measurements of temperature and temperature differences are the White potentiometers, single and double, discussed in Chapter X. The double potentiometers are particularly useful in calorimetry where it is necessary to measure practically simultaneously, two temperatures which

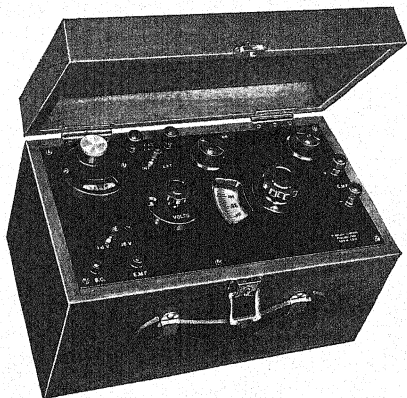


FIG. 34.—Portable precision potentiometer. (*Rubicon Co.*)

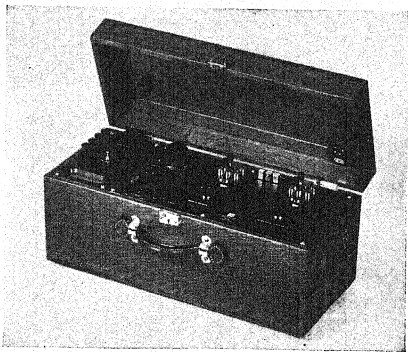


FIG. 35.—Portable precision potentiometer. (*Leeds & Northrup Co.*)

are appreciably different and both changing rather rapidly, but at about the same rate.

For extreme precision there is the Wenner thermocouple potentiometer. The basic principle of this potentiometer has been described (Fig. 33). Its external appearance is illustrated by Fig. 37.

Not all potentiometers use standard cells. A deflection-type potentiometer is illustrated in Fig. 38. A slide wire *A* having a current from a dry cell *B* flowing through it and adjustable by rheostat *C* supplies current to the deflection

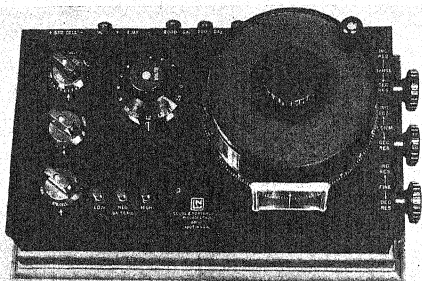


FIG. 36.—Type K-2 potentiometer. (Leeds & Northrup Co.)

instrument *D*. In series with the deflection instrument is a calibration resistor *E*. Connected across *E* in series are a reference junction compensation network *F*, thermocouple *G* and galvanometer *H*. A small dry cell *I* supplies current for the network. This current is adjustable to a definite value by rheostat *J* and indicated by milliammeter *K*. In using the instrument, the resistor *J* is adjusted until the milliammeter deflects to a reference line on its scale. *L* is then adjusted until the galvanometer pointer is on zero. The temperature is then read on instrument *D*. The limit of error of such a portable industrial instrument is less than 0.5 per cent.

In the potentiometer circuit of Fig. 39 the conventional standard cell is replaced by a thermo-cell. This device is a heater and thermocouple in a vacuum tube. The thermocouple has the property of reversing its e.m.f. at a definite temperature of its measuring junction, *i.e.*, for a definite

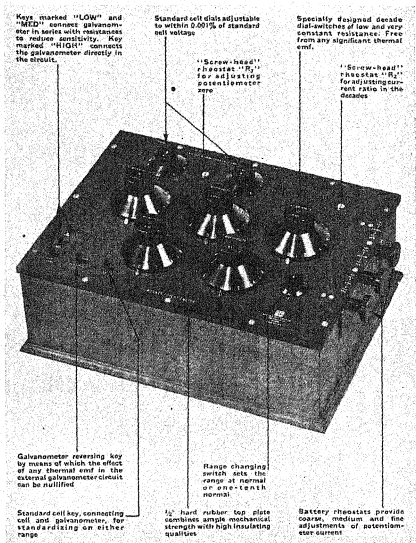


FIG. 37.—Wenner thermocouple potentiometer. (Leeds & Northrup Co.)

current through the heater. Here we have a practical application of the neutral temperature of a thermocouple, discussed in Chap. III. A thermocell, unlike a standard cell, is undamaged by polarization, vibration or freezing and permits use of a more rugged galvanometer. These are

advantages when the instrument is used in aircraft and similar applications.

In another type of deflection potentiometer the galvanometer reflects a beam of light on photoelectric tubes

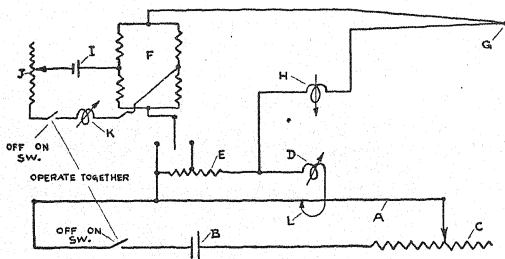


FIG. 38.—Deflection potentiometer. (Lewis Engineering Co.)

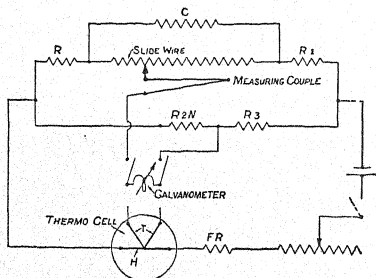


FIG. 39.—Potentiometer using a thermocell. (Lewis Engineering Co.)

and their response is amplified to give a value of the unknown e.m.f. in terms of the reading of a specially-calibrated milliammeter. Figure 40 shows the principle of such a circuit. As actually constructed, an a.c. power supply replaces the batteries shown.

# Summary

The selection of a base- or rare-metal thermocouple, its size and its protection depend on the maximum temperature and the chemical environment to be encountered. To provide a reproducible scale a thermocouple is calibrated at selected fixed points, with: (1) protection from contamination, (2) adequate immersion, (3) constant, known reference junction temperature, (4) pure freezing point sample, and (5) essentially uniform temperature maintained during freezing. The precautions listed as 1-3 are equally essential in

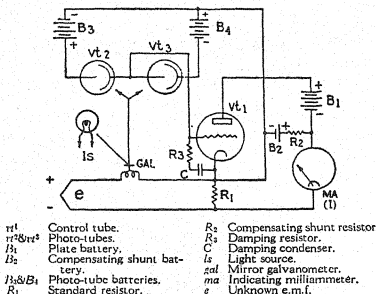


FIG. 40.—Photo-electric deflection potentiometer. (Weston Electrical Instrument Corp.)

the subsequent use of a thermocouple to measure an unknown temperature. The thermal e.m.f. may be measured with a galvanometer, or more accurately with a potentiometer. The latter, being a null method, eliminates the effects of resistance changes in the thermocouple circuit. Using thermocouples of various types, temperature measurements can be obtained over the range from  $-200$  to  $3000^{\circ}\text{C}.$ , although the practical range is much smaller.

# References

- Emmons, H. "Theory and Application of Extended Surface Thermocouples," *J. Franklin Inst.*, 229, 29-52 (1940).



## Problems

1. Is the precision of measurements made with the potentiometer of Fig. 29 affected by (i) contact resistance at  $O$  or  $B$ ? (ii) contact resistance at  $M$  or  $M'$ ? (iii) variation in the e.m.f. of battery  $W$ ? (iv) change in temperature of the part  $MGM'$ ? (v) uniform change in temperature of the entire circuit?
2. What is a cold junction correction?
3. Calculate the e.m.f. of a Pt vs. Pt,Rh thermocouple whose junctions are at  $650^\circ$  and  $1300^\circ\text{C}.$ , respectively. What per cent error results from assuming a linear temperature—e.m.f. relation in making a cold-junction in this case?
4. Answer Prob. 3 for the case of a chromel-alumel couple.
5. Which of the thermocouples of Fig. 23 has the highest thermoelectric power at the melting point of bismuth? Which thermocouple will probably give the highest precision in determining the melting point of bismuth?
6. A millivoltmeter and a recorder, each having a resistance of 100 ohms, are connected to a thermocouple. Should they be connected in series or parallel? Calculate the per cent error in readings for each case, if the line and couple resistance is 4 ohms.
7. What e.m.f. is produced by an iron-constantan thermocouple between  $0^\circ$  and  $80^\circ\text{C}.$ ?
8. A thermocouple and its leads are made of 14 B. & S. Gauge chromel and alumel wires having resistances 0.104 and 0.0432 ohms per foot, respectively. What is the maximum distance that a millivoltmeter may be placed from the couple and not have an error greater than 0.1 per cent in its readings?
9. The hot- and cold-junction temperatures of a thermocouple remain constant. If the resistance of couple and line changes from 2 to 3 ohms the millivoltmeter reading decreases by  $-.33$  per cent. Calculate the resistance of the millivoltmeter.
10. A shunt of 15-ohm resistance is used to compensate for variation in reference-junction temperature of a thermocouple. If the line and couple resistance is 10 ohms, what change in the resistance of the shunt will just compensate for a decrease of 0.3 per cent in the potentiometer reading?
11. Describe the operation of a thermo-cell.

## CHAPTER V

# Radiation

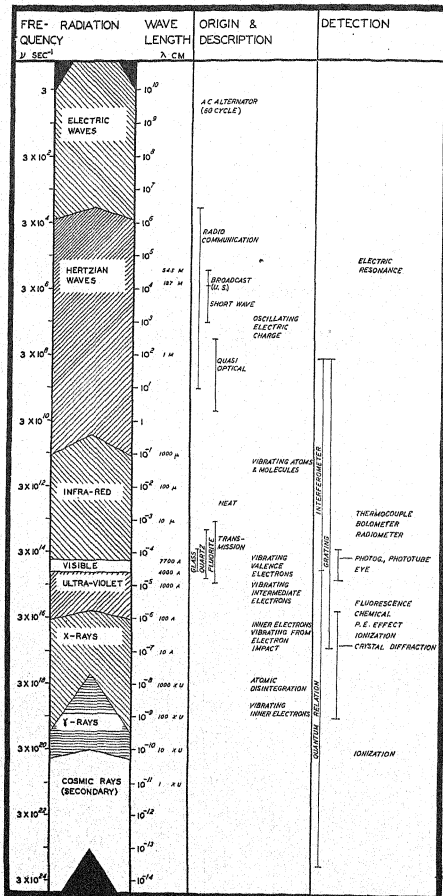
### Introduction

Energy may be transferred from one body to another even though no material substance connects them. A heated body may lose heat even when placed in a vacuum. In such cases the energy in transit is called radiant energy and the process of transfer is called radiation. That this process is distinct from conduction is evident from the fact that it does not require the presence of matter, furthermore material such as copper and wood which are so different in conductivity, cut off heat radiation equally well when placed between source and observer.

Using relatively simple apparatus, such as a sensitive thermopile and a galvanometer as a detector, it is possible to determine the chief characteristics of radiant energy:

1. Rectilinear propagation, according to laws of geometrical optics.
2. Velocity equal to that of light.
3. Propagation through vacuum.
4. Inverse square law of intensity.
5. Reflection, according to same two laws as in optics.
6. Refraction by prisms.
7. Polarization by certain crystals and by reflection.

All these observations lead to the conclusion that radiant energy and light are similar. In fact radiation is used as the more general term, light being that particular kind of radiation which is capable of producing visual sensation. Figure 41 shows that the whole visible spectrum occupies but an exceedingly small part of the whole electromagnetic



“spectrum.” This chart illustrates a major achievement of physics in discovering the fundamental similarity of a number of phenomena which superficially seem unrelated.

The different units used in expressing wavelengths are given in Table I.

TABLE I  
UNITS OF WAVELENGTH

Unit	Symbol	Equivalent to
Micron.....	$\mu$	$10^{-4}$ cm.
Millimicron.....	m $\mu$	$10^{-7}$
Micro-micron.....	$\mu\mu$	$10^{-10}$
Angstrom.....	Å	$10^{-8}$
X-unit.....	X.U.	$10^{-11}$

Prevost of Geneva (1792) was the first to recognize that all bodies emit radiant energy at a rate which increases with the temperature and which is independent of neighboring bodies. The rise or fall observed in the temperature of a body is due to exchange of radiant energy with its surroundings. This is known as Prevost's theorem.

Certain terms needed in a quantitative discussion of radiation will now be defined.

A *blackbody* is defined simply as a body that absorbs all radiation incident upon it (and reflects or transmits none). An equivalent definition is: a blackbody is a radiator which, at any specified temperature, emits in each part of the spectrum the maximum energy obtainable per unit time from any radiator as a result of temperature alone. Radiation from such a body is the standard in terms of which radiation laws are investigated. Like a perfect gas, it is an idealized concept which can be realized only approximately in practice.

*Radiant energy* ( $U$ ) is energy in transit in the form of electromagnetic waves. [Unit: erg.]

*Radiant energy density* ( $u$ ) is the radiant energy per unit volume. [Units: erg cm.<sup>-3</sup>]

*Spectral radiant intensity* ( $J_\lambda$ ) is the radiant energy (of wavelength  $\lambda$ ) per unit wavelength interval emitted per unit time by unit area of a blackbody throughout the solid angle  $2\pi$ , i.e., "hemispherical radiation" [Units: erg sec.<sup>-1</sup> cm.<sup>-2</sup>]

*Radiant intensity* ( $J$ ) is the energy emitted per unit time by unit area of a blackbody throughout the solid angle  $2\pi$ , i.e.,  $J = \int_\lambda J_\lambda d\lambda$ . [Units: erg sec.<sup>-2</sup> cm.<sup>-2</sup>]

*Radiant flux* per unit area, or radiance ( $W$ ) is the radiant energy incident upon unit area in unit time. [Units: watt cm.<sup>-2</sup>]

*Radiant flux* ( $\Phi$ ) is the time rate of flow of radiant energy [Unit: watt].

*Steradiancy* ( $N$ ), a radiant energy term, is the radiant flux per unit solid angle per unit area taken perpendicular to that direction. [Units: watt cm.<sup>-2</sup> steradian<sup>-1</sup>.]

*Total emissivity* ( $e_t$ ) is the ratio of the total radiant flux from a non-blackbody to that from a geometrically similar blackbody at the same temperature. [A numeric.]

*Spectral emissivity* ( $e_\lambda$ ) is the ratio of the monochromatic radiant flux (of wavelength  $\lambda$ ) from a non-blackbody to that from a geometrically similar blackbody at the same temperature. [A numeric.]

The following photometric units are also essential in the study of optical pyrometry:

*Luminous intensity of a source* ( $I$ ) [Unit: international candle].

*Luminous flux* ( $F$ ) is the rate of transfer of luminous energy. [Unit: lumen, which is the flux emitted in unit solid angle by a point source of one candle.]

*Illumination* ( $E$ ) on a surface is measured by the luminous flux incident on unit area. [Units: lux (lumen m.<sup>-2</sup>), foot-candle (lumen ft.<sup>-2</sup>)]

*Brightness* ( $B$ ), a light term, is measured by the flux emitted per unit emissive area as projected on a plane normal to the line of sight. The definition applies both to a self-

luminous body and to one reflecting light. [Unit: lambert (candle cm.<sup>-2</sup>)]

### Total radiation

There are two fundamental laws which describe the radiation from a blackbody. The first, the Stefan-Boltzman law,<sup>1</sup> shows how the total radiant flux from an area  $A$  of a blackbody varies with the temperature:

$$W = \sigma AT^4 \quad (1)$$

Measurements obtained by different observers<sup>2</sup> on an experimental blackbody using a radio-micrometer give an average value of the constant  $\sigma$  as  $5.77 \times 10^{-12}$  watt cm.<sup>-2</sup> deg.<sup>-4</sup>. This law was originally deduced empirically from experimental data by Stefan (1879). Boltzmann gave a theoretical derivation of the law on thermodynamic considerations, treating radiation in a blackbody cavity as analogous to a perfect gas. Another viewpoint is to regard Eq. 1 as a consequence of Planck's law (Eq. 6).

### Monochromatic radiation

The second fundamental law shows how the radiant energy is distributed among the various wavelength intervals,  $d\lambda$ . It required three notable attempts to obtain what is now regarded as the correct form of this law (Eq. 6). Wien<sup>3</sup> derived it in the form

$$J_\lambda = Ac_1\lambda^{-5}e^{\frac{-c_2}{\lambda T}} \quad (2)$$

where  $c_1$  and  $c_2$  are constants. This law fits experimental observations for short wavelengths and low temperatures, but it does not give agreement for large values of  $\lambda T$ .

From Wien's distribution law (Eq. 2), follow two corollaries which show how the maximum intensity of radiation

<sup>1</sup> *Wied. Ann.*, 22, 291 (1884).

<sup>2</sup> R. Ladenberg, *Handbuch der Physik*, vol. 23 (I), p. 20, 1933.

<sup>3</sup> *Ann. Physik*, 58, 662 (1896).

$J_{\lambda m}$  and the wavelength at which it occurs  $\lambda_m$  are related to the temperature

$$\lambda_m T = b \quad (3)$$

$$\frac{J_{\lambda m}}{AT^{15}} = b' \quad (4)$$

Eq. 3 is called Wien's displacement formula.

A law which is satisfactory for long wavelength and high temperature, but not for small values of  $\lambda T$ , was derived by Rayleigh and Jeans<sup>4</sup> in the form

$$J_\lambda = Ac'\lambda^{-4}T \quad (5)$$

Planck abandoned the attempt to secure an adequate radiation law based upon the ideas of classical physics, and introduced his far-reaching quantum hypothesis. This justified the law, previously deduced, which may be expressed in the following alternative forms

$$J_\lambda = \frac{Ac_1\lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} = \frac{8\pi ch\lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} = \frac{8\pi ch\lambda^{-5}}{e^{\frac{h\nu}{kT}} - 1} \quad (6)$$

Here  $c_1$  and  $c_2$  are constants,  $h$  is Planck's constant,  $k$  is the Boltzmann constant,  $c$  the velocity of light,  $\nu$  the frequency of the radiation and  $\lambda$  the wavelength of the radiation. The last three quantities are related by:  $c = \lambda\nu$ .

In order to consider the energy exchanges between radiation and matter, Planck considered a cavity filled with black radiation and the molecules of a perfect gas. Since the exact atomic mechanism of the emission or absorption of radiation was unknown, radiation and gas molecules could not be assumed to interchange energy directly. Planck introduced hypothetical resonators which absorbed energy from radiation and transferred it wholly or in part to molecules which collided with them. In this way thermodynamic

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<sup>4</sup> M. N. Saha and B. N. Srivastava, *A Treatise on Heat*, Allahabad: The Indian Press, 1935.

equilibrium was established. (The important results of Planck's reasoning were later shown to be independent of assumptions as to the exact mechanism assumed for their derivation.)

Planck's resonators were thought of as Hertzian oscillators of molecular dimensions. He showed that

$$u_\nu = \frac{8\pi\nu^3}{c^3} E_\nu$$

where  $u_\nu$  is the energy density of radiation of frequency,  $\nu$  and  $E_\nu$  the average energy of a resonator emitting radiation of frequency  $\nu$ . Planck's innovation was the assumption that the resonators emitted radiation only in integral multiples  $n\epsilon$  of a certain minimum quantity  $\epsilon$ .

The mean energy of these resonators is calculated by classical methods. According to Maxwell's formula, the probability that a particle possesses energy  $E$  is  $e^{-\frac{E}{kT}}$ . Let  $N_0, N_1, \dots, N_s, \dots$  be the number of particles having energy  $0, \epsilon, 2\epsilon, \dots$  respectively. Then

$$N = N_0 + N_1 + N_2 + \dots + N_s + \dots$$

$$E = \epsilon(N_1 + 2N_2 + 3N_3 + \dots)$$

$$N_s = N_0 e^{-\frac{s\epsilon}{kT}}$$

By addition and the substitution  $y = e^{-\frac{\epsilon}{kT}}$ , one obtains

$$N = \frac{N_0}{1 - y} \quad E = N_0 \frac{y}{(1 - y)^2} \epsilon$$

Hence the average energy of a resonator is

$$\frac{E}{N} = \frac{y\epsilon}{(1 - y)} = \frac{\epsilon}{e^{\frac{\epsilon}{kT}} - 1}$$

This value for the average energy differs from the value  $kT$  given by the equipartition law of classical physics.



By considering an adiabatic expansion or compression of radiation, it may be shown that  $\epsilon = h\nu$ . This may be taken as a second assumption in the present discussion. Rayleigh and Jeans showed that the number of oscillators per unit volume in the frequency interval between  $\nu$  and  $\nu + d\nu$  is  $8\pi\nu^2 d\nu / c^3$ . Hence the energy in that frequency interval is

$$u_\nu d\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu$$

or, since  $d\nu = -\frac{c}{\lambda^2} d\lambda$ ,

$$u_\lambda d\lambda = \frac{8\pi c h \lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1} d\lambda$$

which is Planck's law of radiation.

Planck's law agrees with the energy curves obtained by various investigators from experimental blackbodies. For a wide range of temperatures (300°K. to 1700°K.) and a wide range of wavelengths (0.5 $\mu$  to 52 $\mu$ ) this equation represents the observed data to within about 1 per cent. Wien's law gives results accurate to within 1 per cent for values of  $\lambda T < 0.3$  cm. deg. To attain this same accuracy with the Rayleigh-Jeans law,  $\lambda T$  must exceed 77 cm. deg.

The older forms of the radiation laws may be shown to be special cases of Planck's law. Thus if  $\lambda T$  is small,  $e^{\frac{ch}{\lambda kT}} \gg 1$ , and the 1 in the denominator of Eq. 6 may be neglected. It follows that

$$J_\lambda = 8\pi c h \lambda^{-5} e^{-\frac{ch}{\lambda kT}}$$

which is Wien's law. If  $\lambda T$  is large,  $e^{\frac{ch}{\lambda kT}}$  may be expanded in series and it may be shown that

$$J_\lambda = 8\pi \lambda^{-4} kT$$

which is the Rayleigh-Jeans law. Wien's displacement law may be obtained from Planck's law by differentiating  $J_\lambda$  in

Eq. 6 with respect to  $\lambda$  and putting the derivative equal to zero. Finally, if  $J_\lambda d\lambda$  is integrated from  $\lambda = 0$  to  $\lambda = \infty$  an equation identical in form with the Stefan-Boltzmann law results.

Since intensities are not readily calculable from Planck's law, Wien's law has long been used for practical calculations. When, as at high temperatures, accuracy requires the use of Planck's law, calculations may be facilitated by the use of tables.<sup>5</sup> Figure 42 is a comparison of intensity values calculated from Planck's, Wien's and Rayleigh-Jeans' laws

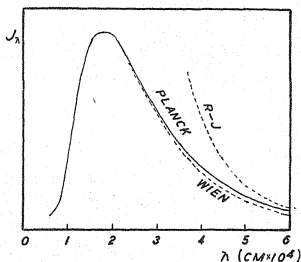


FIG. 42.—Comparison of radiation laws.

for a temperature of 1600°K. It is apparent that the Rayleigh-Jeans law does not give accurate results except for extreme values of  $\lambda T$ . It will be noted from the form of this law that its curve has no maximum and hence predicts radiation of an infinite amount of energy from a given radiator, which certainly is not in accord with experience.

Relations between some of the quantities already defined and Planck's law may be summarized in the following equations

$$dU_\lambda d\lambda = \Phi d\lambda dT = A W_\lambda d\lambda dT = \pi J_\lambda d\lambda dT = \frac{\pi A c_1 \lambda^{-5} d\lambda dT}{e^{\frac{c_2}{\lambda T}} - 1} \quad (7)$$

<sup>5</sup> A. N. Lowan and G. Blanch, *J. Optical Soc. Am.*, 30, 70 (1940).

### Solar constant

A radiation constant of great importance for terrestrial life is the solar constant. This is generally given as the energy that falls in 1 min. upon 1 cm.<sup>2</sup> placed normally to the sun's rays and at the earth's mean distance from the sun. Abbott's value for the solar constant is 1.94 cal. cm.<sup>-2</sup> min.<sup>-1</sup> Individual observations range from 1.85 to 2.02.

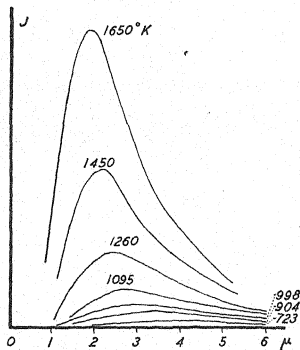


FIG. 43.—Energy distribution for blackbody radiation.

### Lambert's law

The brightness of a blackbody is independent of the direction from which it is observed. This will be the case if for all wavelengths the radiation from a blackbody varies as the cosine of the angle of emission. The approximate validity of Lambert's cosine law for non-blackbodies is important in radiation pyrometry.

The relation between the radiance  $W$  and the brightness  $N$  in a given direction (steradiancy) of a source which obeys Lambert's law is illustrated by Fig. 44. Consider a unit element of surface on the source. Its apparent area in the

direction  $OX$  is equal to  $\cos \alpha$ . The energy emitted in a cone capped by the element of surface  $dS$  taken on a sphere of unit radius, is  $NdS \cos \alpha$ . Since  $dS \cos \alpha$  is the projection

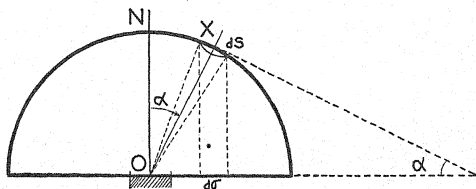


FIG. 44.—Lambert's law.

$d\sigma$  of  $dS$  on the plane of the source, the radiance  $W$  is equal to  $N$  multiplied by the sum of all the elements such as  $d\sigma$ ,  $W = \pi N$ .

### Absorption of radiation

When radiation falls upon a surface, in general part is transmitted, part reflected and the remainder absorbed. Three coefficients of transmission ( $\tau$ ), reflection ( $\rho$ ) and absorption ( $\alpha$ ) are defined as the fractional amount of the incident energy which is, respectively, transmitted, reflected and absorbed. It is evident that

$$\tau + \rho + \alpha = 1 \quad (8)$$

For an opaque body the coefficient of transmission is zero and Eq. 8 reduces to  $\rho + \alpha = 1$ .

From the assumption that the transmission of any body is independent of the intensity of the radiation, it follows that each element of thickness  $dx$  (Fig.

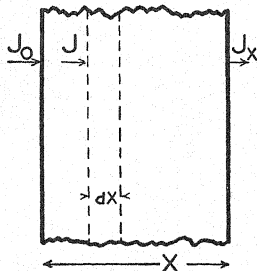


FIG. 45.—Absorption of radiation.

45) in a homogeneous medium will reduce the intensity in the same ratio.

$$\begin{aligned} -dJ_\lambda &= kJ_{\lambda 0} \cdot dx \\ \ln J_\lambda &= -kx \\ \tau_\lambda &= \frac{J_\lambda}{J_{\lambda 0}} = e^{-kt} \end{aligned} \quad (9)$$

When the absorbing medium is a solution, Beer's law states

$$J_\lambda = J_{\lambda 0} e^{-c\beta t} \quad (10)$$

where  $c$  is the concentration of the absorbing substance,  $\beta$  its specific absorptivity and  $t$  the thickness.

### Kirchhoff's law

In an enclosure impermeable to heat and at uniform temperature, the radiation is independent of the form of the enclosure and of bodies placed in the cavity. The radiation is characterized by a spectral brightness which is a function only of wavelength and temperature. It obeys Lambert's law.

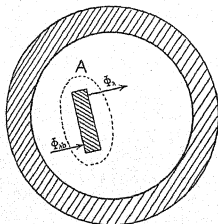


FIG. 46.—Kirchhoff's law.

Consider a body placed in a cavity (Fig. 46) which has attained a temperature equilibrium with it. It receives a radiant flux  $\Phi$  from the cavity, of which it absorbs a fraction  $\alpha$ . Since, for

equilibrium, radiant flux must enter surface  $A$  at the same rate as flux is emitted from that surface,

$$\frac{\Phi}{\alpha} = \Phi_b \quad \text{or} \quad \frac{\Phi_\lambda}{\alpha_\lambda} = \Phi_{\lambda b} \quad (11)$$

which is Kirchhoff's law. It states that at a given temperature the ratio of the radiant flux to the absorptivity is the

same for all bodies and is equal to the radiant flux from a blackbody at the same temperature. A qualitative statement of this law is that good absorbers of radiation are also good radiators.

Kirchhoff's law, together with the Stefan-Boltzmann law modified to apply to a non-blackbody:  $W = e_t \sigma T^4$  give  $\Phi = e_t \sigma A T^4$  and  $e_t \sigma A T^4 / \alpha = \sigma A T^4$  or

$$e_t = \alpha \quad (12)$$

That is, the total emissivity of any radiator is equal to its absorption coefficient for blackbody radiation of the same temperature.

### Experimental blackbodies

The concept of a blackbody, used in the derivation of radiation laws, would have a very limited utility if it were not possible to realize approximate blackbody conditions experimentally. Radiation in an enclosure, say a sphere, after numerous reflections, comes into equilibrium with its surroundings and becomes blackbody radiation. Its intensity for a given wavelength depends only on the wavelength and the temperature and is independent of the material or shape of the enclosure. A small observation hole cut in the sphere will not disturb appreciably this condition, and radiation streaming from it will be (approximately) blackbody radiation. Figure 47 shows two forms of experimental blackbodies: *A* a F ry sphere and *B* a Mendenhall wedge.

Consider the ray sketched in Fig. 47*B*. It contains radiation emitted by the surface at *A*, plus some originating at *B* and reflected at *A*, plus some originating at *C* and reflected successively at *B* and *A*, etc. The intensity of the emerging ray is

$$I_\lambda = \{e_\lambda + e_\lambda \rho_\lambda + e_\lambda \rho_\lambda^2 + \cdots e_\lambda \rho_\lambda^n\} J_\lambda \quad (13)$$

The relation  $e_\lambda = 1 - \rho_\lambda$  may be used to transform Eq. 13 so that all terms in the brackets but the first and last cancel:

$$L_{\lambda} = \{1 - \rho_{\lambda} + \rho_{\lambda} - \rho_{\lambda}^2 + \rho_{\lambda}^2 + \dots - \rho_{\lambda}^n\} J_{\lambda} \cong J_{\lambda b} \quad (14)$$

In practice, if as many as ten reflections are allowed  $\rho_{\lambda}^n$  becomes negligible and the radiation is sensibly blackbody radiation. Ordinary rough oxide coatings approximate this condition.

Measurements of the radiant flux from non-blackbodies are often made with pyrometers and converted into temperature estimates as if the source were a blackbody. Values so obtained are always less than the true temperatures and are called brightness or radiation temperatures.

Most metals when heated radiate in such a manner that their radiation can be color-matched rather closely with that from a blackbody at some temperature. The color

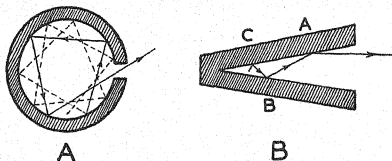


FIG. 47.—Experimental blackbodies.

temperature of a non-blackbody is defined as the temperature of a blackbody whose visible radiation will match in integral color that of the non-blackbody. The radiation temperature, which may differ from the color temperature, is defined as the temperature of a blackbody whose integrated radiation will match that of the non-blackbody.

### Summary

Planck's law  $J_{\lambda} = 8\pi ch\lambda^{-5} \left( e^{\frac{cs}{\lambda T}} - 1 \right)^{-1}$  describes the experimentally-observed distribution of energy vs. wavelength in the radiation from a blackbody, and the dependence of this distribution on temperature. From it can be derived two laws of practical importance in pyrometry: Wien's law for monochromatic radiation and the Stefan-Boltzmann law

for the total radiation as a function of temperature. Lambert's law states that the brightness of a blackbody is independent of the angle at which it is observed. Kirchhoff's law is a mathematical statement of the fact that good absorbers of radiation are also good radiators. It suggests that blackbody radiation may be obtained practically by the use of a cavity source in which multiple reflections occur. Radiation is usually absorbed according to an exponential law:  $J_\lambda = J_{\lambda 0}e^{-kt}$  in media which only partially transmit it.

## References

- Forsythe, W. E., Ed. *Measurement of Radiant Energy*, New York: McGraw-Hill, 1937. 452 pp.
- Forsythe, W. E. "Intercomparison of the High Temperature Scale," *Phys. Rev.*, 38, 1247-53 (1931).
- Luckiesh, M. Several books on color, New York: Van Nostrand.
- Ribaud, G. *Le rayonnement des corps non noirs*, Paris, 1929.
- Richtmyer, F. K. *Introduction to Modern Physics*, New York: McGraw-Hill, 1928. pp. 221-247.

## Problems

1. Show that for small values of  $\lambda T$  Planck's law reduces to Wien's law, while for large values of  $\lambda T$  it reduces to the Rayleigh-Jeans law.
2. Derive Wien's displacement law from Eq. 6.
3. Calculate the ratios of intensities of monochromatic radiation  $J_{1600}/J_{1000}$  as the temperature of a blackbody is increased from 1000°C. to 1600°C., considering (i)  $\lambda = 0.4\mu$  and (ii)  $\lambda = 0.6\mu$ .  
Comment on your answer with reference to Fig. 43.
4. Taking Abbot's value of the solar constant, the radius of the sun as  $4.3 \times 10^5$  miles and the diameter of the earth's orbit as  $1.86 \times 10^8$  miles, calculate the temperature of the sun assuming it to be a blackbody.
5. A bather lies on a sunny beach. Calculate the approximate energy of the radiation received by the bather's body in 1 hr. List all assumptions made.
6. Which of the substances listed in Table XX most closely approximate a blackbody? Explain.
7. Compare the relative power supplies necessary to maintain a furnace at temperature of 1000°C. and 2000°C., using the Stefan-Boltzmann law.



8. State the relation between the emissivity, the reflectivity and the absorptivity of a surface.
9. A blackened copper sphere of diameter 10 cm. is cooled in an evacuated enclosure whose walls are kept at  $0^{\circ}\text{C}$ . In what time does its temperature change from  $228^{\circ}$  to  $227^{\circ}\text{C}$ .? (Show that heat lost per sec.  $= \frac{4}{3} \pi r^2 \rho C \frac{dT}{dt} = 4\pi r^2 \sigma (T^4 - T_0^4)$ .)
10. How many reflections are required in (i) a platinum cavity, (ii) a carbon cavity to reduce the intensity of an entering light beam to 5% of its initial value?
11. A piece of incandescent carbon at  $2000^{\circ}\text{K}$ . is seen reflected from a clean platinum surface at the same temperature. How does the sum of the normal platinum and the reflected carbon brightness compare with that of a blackbody at  $2000^{\circ}\text{K}$ .?
12. The operating temperature of a tungsten filament in a lamp bulb (evacuated) is  $2450^{\circ}\text{K}$ . and its emissivity is .30. Find the surface area of the filament of a 25 w. lamp.
13. Compute the number of quanta of radiation from a sodium lamp ( $5890\text{\AA}$ ) required to make an erg of energy.
14. Calculate the power (watts  $\text{cm}^{-2}$   $\text{sec}^{-1}$ ) reaching the receiver of a total radiation pyrometer which subtends a solid angle of 0.01 of a black-body source whose temperature is  $1000^{\circ}\text{K}$ .
15. An optical pyrometer is sighted through a window of absorption coefficient  $\mu$  and thickness  $x$  on the surface of a metal which has emissivity  $e_{\lambda}$ . Derive the relation between the true temperature of the metal  $T_t$  and the temperature indicated by the optical pyrometer  $T_a$ .
16. A radiation pyrometer is sighted through a "gray" window of absorption coefficient  $\mu$  and thickness  $x$  on the surface of a molten metal which has a total emissivity  $e$ . Derive the relation between the true temperature of the metal  $T_t$  and the temperature indicated on the pyrometer  $T_a$ .

## CHAPTER VI

# Radiation Pyrometry

### Introduction

The temperatures of very hot bodies have long been judged visually by their color or brightness. Table I is a color scale of temperature. With practice one can probably estimate temperatures visually to within  $50^{\circ}\text{C}$ . Thus it may be said that temperatures were estimated by Wiens' displacement law long before that law was explicitly formulated (Fig. 48).

TABLE I

Color	Degrees centigrade	Degrees Fahrenheit
Lowest visible red.....	475	887
Dull red.....	550-625	1022-1157
Full cherry red.....	700	1292
Light red.....	850	1562
Orange.....	900	1652
Full yellow.....	950-1000	1742-1832
White.....	1150 and up	2102 and up

Direct visual estimation of temperature is, naturally, only approximate and has all the uncertainties of a purely subjective method. Instruments which permit quantitative measurement of temperature in terms of radiation either provide the human eye with a standard comparison body or contain a sensitive element which makes visual observation unnecessary.

The Stefan-Boltzmann law and Wien's radiation laws, which describe the manner in which the radiation emitted

from a hot body varies with the temperature, suggest three ways in which radiation can be utilized in pyrometry. A pyrometer may be designed to measure as heat the radiation of all wavelengths emitted by the source. Such an instrument is called a total radiation pyrometer, or more often merely a radiation pyrometer. A pyrometer may be responsive to the intensity of radiation only in a narrow band of wavelengths, usually in the visible spectrum. It is then called



FIG. 48.—The first optical pyrometer. (*H. T. Wensel.*)

a partial radiation pyrometer and may be of either the optical or photoelectric type. A third type of instrument is a color pyrometer which indicates temperature from the relative intensity of radiation at two different wavelengths, usually in the red and green.

### Total Radiation Pyrometers

#### Principle of operation

In most total radiation pyrometers a convex lens or concave mirror concentrates a fraction of the radiation from the

test body on a sensitive element which has a blackened receiving surface. The sensitive element may be a bimetallic spiral, a platinum foil whose resistance changes with temperature, a small bar whose magnetic permeability varies with temperature, a thermocouple or a thermopile. In the common type of radiation pyrometer the e.m.f. of a thermocouple is used to actuate a galvanometer. Calibration is done empirically with the aid of a blackbody, and the pyrometer scale marked to indicate temperature directly.

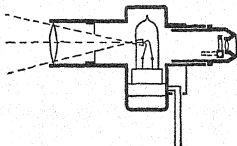


FIG. 49.—Total radiation pyrometer. (Bacharach Industrial Instrument Co.)

A total radiation pyrometer for use as a portable instrument is illustrated in Fig. 49. The receiver, a blackened platinum foil, and the thermocouple are mounted in an evacuated tube for protection and to avoid the effect of convection currents. Sighting the instrument is done through an ocular

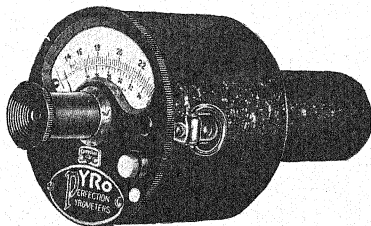


FIG. 50.—Total radiation pyrometer. (Pyrometer Instrument Co.)

lens. The eye is protected by a red filter. The thermocouple e.m.f., and hence the temperature, may be read on an auxiliary galvanometer or used to operate a recording instrument.

A self-contained type of total radiation pyrometer is illustrated in Fig. 50. The galvanometer can be clamped in

its deflected position and read after the sighting telescope has been lowered from the eye.

One type of fixed-focus radiation pyrometer uses a conical mirror to gather radiation and concentrate it on a receiver placed near the apex of the cone. No optical device is needed for sighting the pyrometer. It is held in the hand and pointed toward the test body until the millivoltmeter reaches a maximum deflection. This type of instrument does not give visual assurance that the dimensions of the

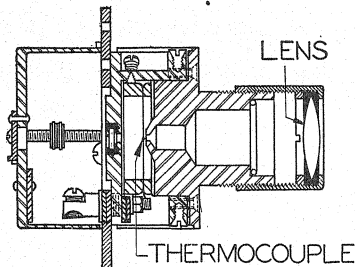


FIG. 51.—Total radiation pyrometer. (*Leeds & Northrup Co.*)

source are large enough so that its image completely covers the receiver.

Many total radiation pyrometers are used in permanent installations for checking or recording the temperature of furnaces and ovens. A pyrometer for such applications (Fig. 51) is sealed in a case which protects it from dust, moisture and stray radiation. Provision is made for adjusting the temperature range and for focusing the pyrometer if it is to be used at a distance less than the "fixed focus" distance.

To an increasing extent in recent years, the radiation pyrometer has become an accepted industrial pyrometer for certain types of measurement. Its use is well established in at least eight types of service: where (1) vibration or (2)

corrosion ruins couples; where (3) the work or (4) the furnace moves; where (5) protecting tubes make couple response too slow; (6) where temperature is above thermocouple range; (7) where the temperature gradient between work and couple fluctuates; and (8) where maintenance of couples (usually but not always platinum) is excessive.

### Change of range

In measuring very high temperatures with a radiation pyrometer it is customary to intercept part of the radiation with a diaphragm placed in front of the pyrometer opening, and then recalibrate the pyrometer. Thus the instrument itself need not be subjected to a detrimental increase in temperature. By having two scale ranges on the galvanometer its deflections may be read more accurately. The temperatures  $T_1$  and  $T_2$  of a source when viewed through diaphragm areas  $A_1$  and  $A_2$  respectively, for a given galvanometer deflection are related by the Stefan-Boltzman law

$$A_1 T_1^4 = A_2 T_2^4 \quad (1)$$

### Effect of distance

It is necessary that the image of the radiating source be properly focused in the radiation pyrometer, i.e., the source and the sensitive element should be at conjugate foci of the lens or mirror. Furthermore, for lens-type detectors, the image should cover completely the receiving disk (Fig. 49) or the opening in the shield placed over the thermocouple (Fig. 51). This condition will be satisfied for only one distance of the object, for a given position of the lens with respect to the receiving disk. For any other distance, the image will be out of focus, and the temperature measurement will be in error. If the instrument is focused for a distance twelve or more times the focus length of the lens, it is usually sufficiently well in focus for greater distances.

In a mirror-type radiation pyrometer, it is the image of the front diaphragm which is focused on the receiving disk. In general, the disk is not completely covered. The measured

temperature is independent of object distance, provided the object is large enough to completely fill the field of view of the pyrometer.

Ribaud has investigated experimentally the influence of the size of the image on the readings of a total radiation pyrometer, using a sheet of oxidized nickel, uniformly heated electrically, as the source. The e.m.f. increased appreciably (about 20 %) as the size of the image increased from 0.15 cm. (diameter of the receiver) to 1 cm. If the instrument were calibrated with an image diameter equal to 4 mm. errors of 2 % and 11 % would result in the e.m.f. read with images of 10 and 2 mm., respectively. These errors appear because the radiation which is not intercepted by the thermocouple heats the surrounding walls resulting in their radiating toward the receiver. This effect increases with the size of the image.

### Calibration

The calibration of a total radiation pyrometer is effected by directing it toward an electrically-heated cavity which approximates a blackbody. The temperature of the furnace is obtained from a partial radiation pyrometer or a thermocouple, and the corresponding e.m.f. for the total radiation pyrometer noted. This calibration requires a source of relatively large volume held at uniform temperature. It is more difficult than the calibration of a partial radiation pyrometer. A graphite muffle or a porcelain tube provided with diaphragms can be made to approximate a blackbody. A slow circulation of air avoids the accumulation of carbon dioxide in the path of the radiation.

### Sources of error

Radiation pyrometers are more difficult to use accurately than appears at first glance. They are calibrated for blackbody conditions. When a pyrometer is sighted on a furnace cavity of uniform temperature the radiation which it receives is approximately blackbody radiation. When, however,

radiation pyrometer readings are taken on a test body in the open, the measured temperature  $T_a$  is lower than the true temperature  $T$  by an amount which depends upon the emissivity of the surface. The amount of such discrepancy can be calculated from the Stefan-Boltzman law provided the emissivity  $e_t$  is known,

$$e_t \sigma A T^4 = \sigma A T_a^4$$

$$e_t = \frac{T_a^4}{T^4} \quad (2)$$

The emissivities of many non-blackbodies are small and inaccurately known. Radiation pyrometer measurements on such materials are unreliable. Fortunately in many industrial processes it is sufficient to be able to reproduce certain temperature conditions without the necessity of measuring the temperatures with high accuracy. For such application a radiation pyrometer is satisfactory provided merely that its calibration remains constant.

### Industrial measurement

A closed-end tube inserted in a furnace or molten bath can serve as a blackbody target for radiation pyrometer measurements. It also eliminates the effect of flames or absorbing gases. By extending the reasoning discussed in deriving Eq. V.14 it is possible to calculate the ratio of length to diameter necessary for a cylindrical tube of known emissivity to approximate any desired degree of "blackness" (Table II).

TABLE II<sup>1</sup>

RATIO OF LENGTH TO DIAMETER FOR A CYLINDER OF 99% BLACKNESS

Length/diameter	Emissivity of tube		
	0.75	0.50	0.25
First approximation.....	3.8	5.8	9.0
Second approximation.....	4.8	7.0	10.7

<sup>1</sup> H. Buckley, *Phil. Mag.*, 17, 576 (1934).



In some applications, such as on glass furnaces, the pyrometer may be sighted directly on the molten surface whose temperature it is desired to measure. Even then the use of an open-end sighting tube through which a current of air is forced is an advantage in removing absorbing gases. Radiation pyrometers are by no means limited in their application to measuring temperatures of molten materials. They are frequently sighted on material being heat-treated, stock being hot-rolled, or on the linings of furnaces, kilns, etc.

Errors due to the heat radiated from the pyrometer to the thermocouple increase with the size of the image of the source. They are greater in instruments using glass mirrors than in those using metallic mirrors because of the poor thermal conductivity of glass. Instruments provided with glass or quartz lenses which are absorbing in the infra-red are subject to errors due to their heating. Such errors are minimized by using the instrument with the image of the same size as that for which it was calibrated. Water-cooling of the instrument case and the use of a fluorite lens practically eliminate this cause of error.

## Partial Radiation Pyrometers

### Principle of operation

The idea of an instrument employing Wien's law to measure temperatures was suggested by Le Chatelier (1892). Most partial radiation pyrometers rely on visual observations. Some employ phototubes. The human eye can judge the equality of two illuminations of the same color with high precision, but not their ratio. This characteristic of the eye is taken into account in the design of many types of precision scientific instruments, such as photometers, colorimeters and polarimeters, in which the eye is required only to observe when two parts of a divided field of view are matched.

An optical pyrometer may be regarded as an instrument designed to improve visual estimates of temperature by

providing the eye with a comparison source. The comparison source is a lamp filament. The filament is connected in series with a battery, resistor and milliammeter. By varying the current through the filament it may be made to match in brightness the image of the hot body on which the pyrometer is sighted. The temperature of the test body is then determined from a reading of the milliammeter and a calibration curve provided for the lamp used. In an alternative design of optical pyrometer the filament current is kept constant and a match obtained by varying the amount of radiation from the source which is admitted to the eyepiece.

Temperatures might be measured with an optical pyrometer using the whole visible spectrum. If that were done errors would be introduced and observers would differ widely in their readings owing to the color difference between the filament and the source being examined. Greater accuracy is obtained if a so-called monochromatic filter is used in the eyepiece. This is usually a glass which transmits a narrow band of wavelengths ( $0.005$  to  $0.01\mu$  wide) in the red ( $0.63$  to  $0.67\mu$ ). Red screens are chosen for the following reasons: (i) At low temperatures red radiation first becomes visible and hence readings may be made at slightly lower temperatures with red glass. (ii) Subjectively the color change with wavelength seems much less in the red than in the green. (iii) Better visual monochromatism can be obtained for glasses of this color because the visibility curve fixes the cut-off at the long wavelength end of the red band, and the glass is required to cut off only the short wavelength end of the spectrum.

Truly monochromatic screens are nonexistent. If they were available, the very limited intensity which they could transmit would make them of doubtful value in practical optical pyrometry. In using a pyrometer with a screen which is only approximately monochromatic, it is the integral luminous intensity through the screen, of the source examined (at one temperature) and of the pyrometer filament (at a

lower temperature) that are compared. For this reason the effective wavelength  $\lambda_{T_1 T_2}$  of the screen has been defined as the wavelength for which the ratio  $Z$  of the spectral brightness of two blackbodies at temperatures  $T_1$  and  $T_2$  is equal to  $z$ , the ratio of the total fluxes which they send through the screen.

### Change of range

An optical pyrometer may be adapted to measure temperatures higher than the maximum operating temperature of its filament by interposing one or more absorbing screens between the objective and the filament. The thickness  $x$  of filter having an absorption coefficient  $k$  needed to change the pyrometer range by a specified amount can be calculated by combining the expression for Wien's law with that used in defining an absorption coefficient.

$$e^{-kx} = \frac{c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T_a}}}{c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}} \quad (3)$$

Performing the division indicated and taking the logarithm of each side of the equation we obtain

$$\frac{1}{T} - \frac{1}{T_a} = - \frac{k\lambda x}{c_2} \quad (4)$$

where  $T_a$  is the apparent temperature of a blackbody of temperature  $T$  when viewed through a screen of thickness  $x$  having an absorption coefficient  $k$ .

### Effect of distance

Temperature measurements made with a partial radiation pyrometer are independent of the sighting distance, subject to the restrictions mentioned for total radiation pyrometers.

### Glowing filament pyrometers

In a Morse type optical pyrometer, Fig. 52, an objective lens focuses a real image of the furnace opening or other

source in the plane of a standard lamp filament. Both image and filament are magnified for the observer by an ocular lens. The current is varied until the filament matches the background illumination. The calibration of the instrument gives the temperature of the test body in terms of the filament current. The uncertainty of measurements made with such an instrument is of the order of  $10^{\circ}\text{C}$ . Its accuracy is limited usually by the milliammeter rather than by the sensitivity of the eye in judging a photometric match. A common

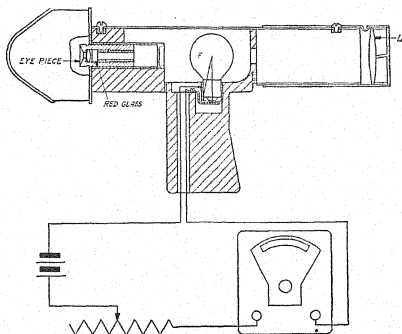


FIG. 52.—Glowing filament optical pyrometer. (Leeds & Northrup Co.)

source of failure of the milliammeter is the accumulation of iron dust on the coil and the pole faces of the meter.

In precision laboratory optical pyrometers, a potentiometer is used for measuring the lamp current. A potentiometer circuit has been adapted for use in a portable optical pyrometer<sup>2</sup> in the form diagram in Fig. 53. The current through the pyrometer lamp  $L$  is adjusted with the slidewire rheostat  $A$  when the switch  $S$  is closed. The current from the battery flows through the shunted potentiometer slidewire  $R$  and the

<sup>2</sup> R. C. Machler, *Rev. Sci. Instruments*, 10, 386 (1939).

resistor  $C$ . The potentiometer slidewire can be considered as being a variable shunt, the resistance of which is adjusted so that the product of the lamp current  $I$  and the shunt resistance equals the e.m.f.  $e$  of the standard cell  $E$ . For potentiometer balance

$$I \left\{ \frac{\alpha R R'}{(R + R')} + R_c \right\} = e \quad (5)$$

where  $\alpha$  is the fraction of the potentiometer slidewire included in the potentiometer shunt.

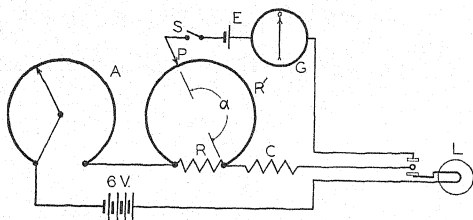


FIG. 53.—Potentiometer circuit for portable optical pyrometer.

It is evident from Eq. 5 that for  $\alpha = 0$

$$I_{\max} = \frac{e}{R_c}$$

and for  $\alpha = 1$

$$I_{\min} = \frac{e}{\frac{R R'}{(R + R')} + R_c}$$

from which  $R_c$  and the shunted value of  $R$  can be determined for a lamp which requires known  $I_{\max}$  and  $I_{\min}$  to cover the temperature range. The scale associated with contact  $P$  can be calibrated in milliamperes or in temperature. Thus has been provided a direct-reading potentiometer instrument, fully adapted for plant use, which offers

many advantages not possessed by the earlier milliammeter-type instruments.

The lamp is operated with currents ranging from 20 to 60 ma. The galvanometer is sufficiently sensitive to detect a 0.1% unbalance of the potentiometer which corresponds to approximately  $1^{\circ}\text{C}$ . A further increase in accuracy of temperature readings cannot be expected by making the current measurements more accurate, since the photometric match cannot be made consistently to better than 1%, which cor-

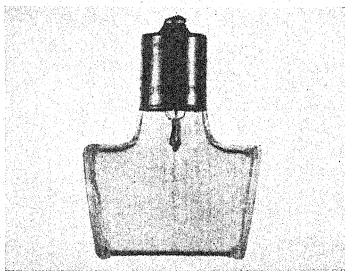


FIG. 54.—Pyrometer lamp. (W. E. Forsythe, *J. Applied Physics*, 11, 408 (1940).)

responds to a temperature uncertainty of the order of  $1^{\circ}\text{C}$ . in the low range of the instrument.

The rheostat and potentiometer slidewire contacts are coupled mechanically with a friction clutch so that when the rheostat contact is moved to adjust the current the potentiometer contact is carried with it in the direction required to maintain potentiometer balance, but when the potentiometer contact is operated by its knob the rheostat contact remains at rest. This device facilitates manipulation of the instrument and protects the standard cell from unnecessary currents.

Improvements in lamp design as well as in current-measuring circuits have contributed to the increased accuracy

of modern optical pyrometers. The pyrometer lamp (Fig. 54) should have a very clear glass bulb and, for the most accurate work, should have plane glass windows on both sides. These windows should not be perpendicular to the axis of the telescope but should be mounted at an angle of about 15° from perpendicularity so as to avoid reflecting images of the filament into the field of view. The vacuum in the bulb

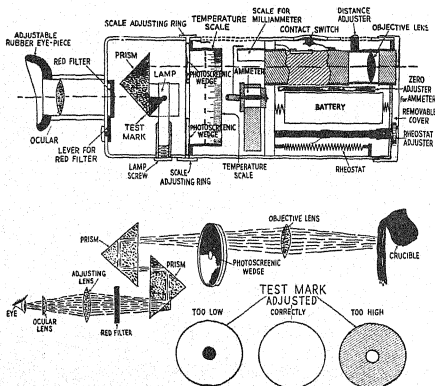


FIG. 55.—Optical pyrometer. (Pyrometer Instrument Co.)

should be the best obtainable. A tungsten filament if not used above the melting point of palladium ( $1828^{\circ}\text{K.}$ ) will last almost indefinitely, and any failure will probably be due to accident rather than to any deterioration in the filament.

### Gray wedge pyrometers

Figure 55 illustrates a compact type of gray wedge optical pyrometer. The filament current is adjusted with the aid of the rheostat and milliammeter to the value for which the lamp was calibrated. Then, with the pyrometer sighted on a

hot body, the circular wedge is rotated until the brightness of the incident radiation is reduced to match the brightness of the comparison lamp. The temperature is read directly from the scale affixed to the wedge. The appearance of the field of view is indicated in the lowest part of the diagram. Owing to the red filter in the eyepiece the comparison is made with approximately monochromatic light and does

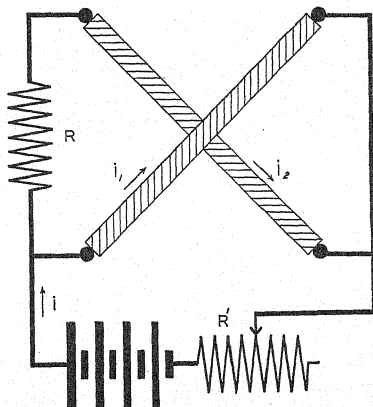


FIG. 56.—Circuit for crossed-filament optical pyrometer.

not depend upon the observer's color vision. The range of the instrument can be changed by inserting another absorbing screen between the source of radiation and the comparison lamp in the pyrometer.

In a laboratory type gray wedge pyrometer designed by Ribaud the constancy of the filament temperature is indicated by measuring the filament resistance on a Wheatstone bridge. The radiation from the source is reduced to match that of the filament by a progressive gray filter like that described above.



The accuracy attained by such an instrument is limited by the ability of the eye to judge the equality of the two illuminations. This uncertainty is only about  $1^\circ$  at  $1000^\circ\text{C.}$  and  $2^\circ$  at  $2000^\circ\text{C.}$

### Gray wedge, crossed-filament pyrometer

In a novel type of pyrometer two crossed filaments of different resistances are combined in one lamp (Fig. 56). Control of the current by an external variable resistor changes the brightness of the filaments. For only one particular value of the current are both filaments equally bright. This gives a fixed reference temperature. By means of a graduated gray wedge between the objective lens and the lamp the radiation of the test body is decreased to match that of the filaments. The edge carries a scale calibrated to read temperature. This pyrometer dispenses with the need for a milliammeter. Technical difficulties in the manufacture of the crossed-filament lamps have retarded the industrial use of this type of pyrometer.

### Photoelectric pyrometers

In a photoelectric pyrometer the radiation from a hot body is directed on a phototube and causes it to pass a current which bears a definite relation to the temperature of the test body. This current is amplified by an especially stable vacuum tube amplifier and the amplified current is used to actuate an indicator, recorder or controlling instrument. The principle advantages of such a pyrometer are its rapid response and the fact that it can be used to provide continuous temperature records.

A vacuum type phototube with a caesium-oxygen-silver cathode is employed in the photoelectric pyrometer. While such a tube is far less sensitive than a gas-filled tube, it is also much more stable. In Fig. 57 are shown energy vs wavelength curves of the same type as in Chap. V, Fig. 43. In addition there is shown in Fig. 57 a curve of the relative response of a phototube to radiations of various wavelengths.

The relative response of the phototube to radiation from a body at various temperatures may be found by multiplying

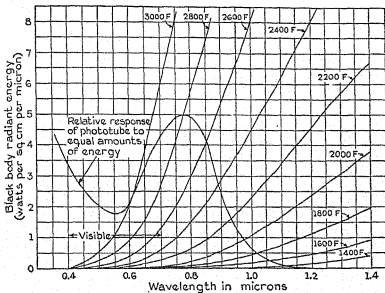


FIG. 57.—Blackbody radiation and phototube response. (W. R. King, *Gen. Elec. Rev.*, 39, 526 (1936).)

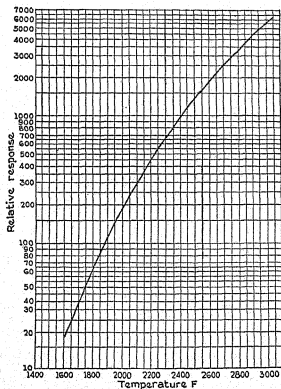
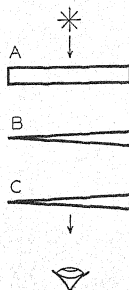


FIG. 58.—Relative phototube response to blackbody radiation. (W. R. King, *Gen. Elec. Rev.*, 39, 526 (1936).)

the ordinates of the phototube response curve by the ordinates

under the curve resulting from the plotting of these products against the wavelength is the relative phototube response for the temperature represented by the radiation curve used. If this process is carried out for a number of temperatures, a curve of relative phototube response for various temperatures may be obtained by plotting the areas against the temperatures. Such a curve is shown in Fig. 58.

Data taken on a number of vacuum type phototubes indicate that variations in sensitivity over a period of 1000 hr. are, at worst, around ten per cent, and that these variations are relatively slow. Reference to Fig. 58 will show that a 10 per cent variation in phototube response corresponds to only a small error in temperature.



Color pyrometers

FIG. 59.—Schematic diagram of a color pyrometer.

In many applications of practical importance it is desired to make temperature determinations with an optical pyrometer on test bodies whose emissivities are not accurately known. The temperature indicated by a conventional optical pyrometer is less than the true temperature by an unknown amount. If the temperature can be determined as a function of the relative intensities of radiation of two colors,  $J_\lambda/J_{\lambda'}$ , the difficulty associated with the unknown emissivity is greatly reduced. The uncertainty is not

entirely eliminated since the emissivity may be slightly different for the two colors, being generally greater for shorter wavelengths. A color pyrometer is designed to facilitate such measurements.

Consider that filter *A* in Fig. 59 transmits only two colors, say red and green. Filter *B* is a wedge which absorbs red in gradually increasing amounts. Filter *C* is a wedge which absorbs green in gradually increasing amounts. If filters *B* and *C* were absent the eye would receive a mixture of red and

green radiation. For a certain temperature of the source this mixture would match an arbitrary standard, say white, and would appear red or green at temperatures respectively higher or lower. Suppose that when the source is viewed through filter *A* a green tint is observed. Then by adjusting the position of *B* or *C* the absorption of green can be increased until the tint becomes white. If *B* absorbs more strongly than *C*, the filters can be joined rigidly and moved together to obtain the desired effect. In practice the three filters are joined and the compound filter moved with respect to an eyepiece, simultaneously moving a pointer along a scale calibrated in temperatures.

The highest temperature thus measured is about  $3000^{\circ}\text{C}$ . A range of 500 to  $2000^{\circ}\text{C}$ . is ordinarily sufficient. Practically, the lower limit of temperature depends upon the colors chosen. For bright metals of low emissivity the limit is  $600^{\circ}\text{C}$ . for red,  $750^{\circ}\text{C}$ . for yellow,  $900^{\circ}\text{C}$ . for green and  $1000^{\circ}\text{C}$ . for blue.

Physiological considerations require that for high accuracy colors be used which provide marked change in tint on each side of the standard setting. It is best to use complimentary colors, taking white as the standard for reference. Readings are influenced by the effect on the eye of brightness and fatigue and by the sensitivity of the eye to color. Partial color blindness can be compensated for by appropriate choice of filters.

The filters of the original color pyrometers were organic dye solutions in glass cells. In the portable instrument<sup>3</sup>



FIG. 60.—Color pyrometer. (Pyrometer Instrument Co.)

<sup>3</sup> G. Naeser, *Arch. Eisenhüttenw.* 9, 483 (1935).

pictured in Fig. 60 glass filters are used. The optical system is constructed to provide a divided field of view. An arrow appears against the image of the test body. The position of the filters is changed by rotating two knurled rings until the arrow blends with the image in the same shade of color. One scale gives the true (color) temperature of the object under consideration whereas a second scale is calibrated for blackbody conditions. Under truly blackbody conditions

the two scale readings are identical. It is apparent that the color pyrometer can be used to obtain temperatures of bodies of unknown emissivity and even to estimate their emissivities.

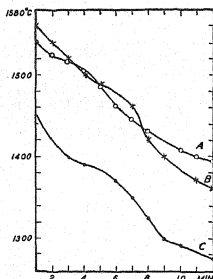


FIG. 61.—Cooling curves obtained with (A) thermocouple, (B) optical pyrometer, (C) color pyrometer.

Figure 61 is an interesting comparison of three methods commonly used in measuring steel temperatures. The curves A, B and C are cooling curves for molten iron obtained respectively with a Pt-PtRh thermocouple in a 2 mm. protecting sheath, an optical pyrometer and a Naeser color pyrometer. The instruments were checked before and after the experiment at the gold

point. The color pyrometer indications are probably accurate to within one or two per cent.

### Photoelectric color pyrometer

A pyrometer<sup>4</sup> which combines the advantages of a color pyrometer with those of photoelectric (continuous) detection is illustrated in Fig. 62. The radiation from the source is split into red and green beams, the ratio of whose intensities is dependent only upon the temperature of the source. These two colored beams are received simultaneously by two photo-

<sup>4</sup> H. W. Russell and C. F. Lucks in *Temperature—Its Measurement and Control* . . . pp. 1159-1163.

electric cells, and the ratio of the output currents provides a direct indication of the temperature. This current ratio is determined by a Wheatstone network (Fig. 63) in which resistances of variable ratio are adjusted to give zero potential

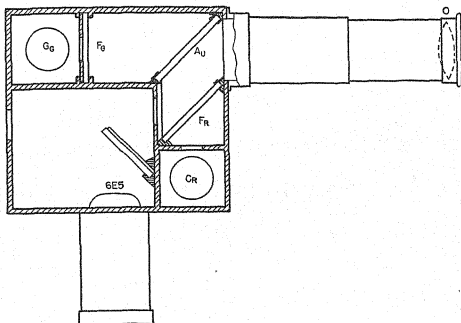


FIG. 62.—Schematic diagram of head for portable two color photoelectric pyrometer.

between their outer terminals. In a manually operated form of the instrument a variable high resistance is used and a

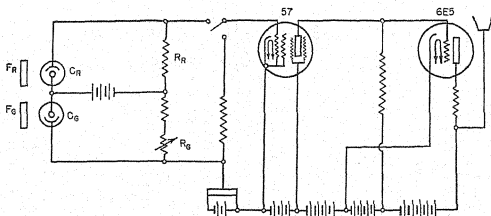


FIG. 63.—Circuit diagram for portable two color photoelectric pyrometer.

6E5 "visual tuning" vacuum tube is used as the null indicator. In an automatic recording form of the instrument the photoelectric cell currents are amplified by tubes in the pyrometer

head, and the variable ratio resistances are in a remote self-balancing recorder. The instruments are operative on sources having temperatures in excess of  $1000^{\circ}\text{C}$ . For measurements made under "gray" conditions, i.e.,  $\epsilon_{\text{red}} = \epsilon_{\text{green}}$ , the temperatures indicated are accurate to within  $10^{\circ}\text{C}$ .

### Effect of absorption

If the radiation from a test body undergoes any absorption before reaching the pyrometer the reading indicated by the instrument will be lower than the true temperature. The effect of smoke, moisture and carbon dioxide, which absorb in the infra-red, is not as detrimental on the reading of a partial radiation pyrometer as in the case of a total radiation pyrometer.

It is occasionally desirable to introduce a sheet of glass or a totally reflecting prism between the source and the objective lens of a partial radiation pyrometer. When light is incident normally on a glass surface approximately 4 per cent is reflected. The transmission factor for a clear glass plate or prism is therefore about 0.92. A temperature  $T_a$  indicated by a pyrometer sighted through a clear glass plate then requires a correction  $\Delta T$  determined from the relation

$$\frac{\Delta T}{T^2} = \frac{\lambda}{c_2} \text{antilog } 0.92 = 38 \times 10^{-7} \text{ (for } \lambda = 0.65 \text{)}$$

The transmission factor is nearly independent of the angle with the normal up to  $40^{\circ}$ , and then falls off rapidly from 0.92 to about 0.50 as the angle of incidence increases from  $40^{\circ}$  to  $75^{\circ}$ . If the transmission factor is known, the correction to be applied to the pyrometer reading may be obtained conveniently from Fig. 64.<sup>5</sup> If the glass shows color there will be additional absorption losses that cannot be obtained from the chart and which must be determined experimentally.

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<sup>5</sup> F. Benford, *J. Optical Soc. Am.* 29, 162 (1939).

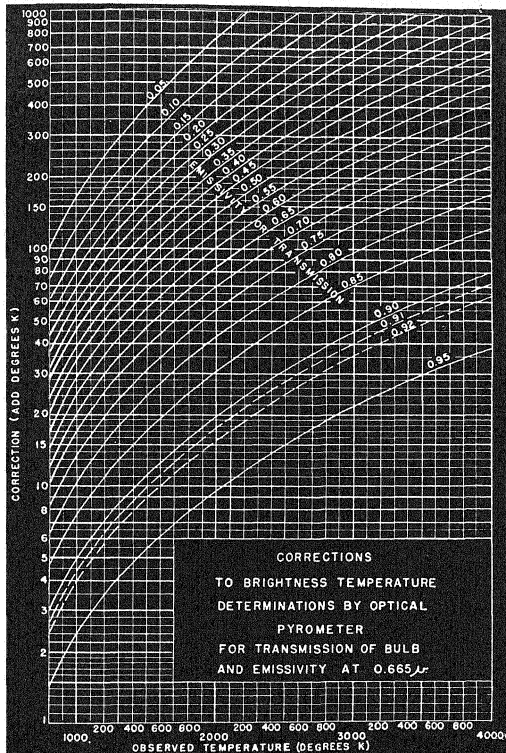


FIG. 64.



### Disappearance of filament

For precision measurements with a disappearing filament pyrometer one might suppose that it is important to have the filament appear uniformly brilliant without dark or bright fringes at its borders. The fringes frequently observed have been variously attributed to reflection of light of the test body from the filament, diffraction effects, and the failure of Lambert's cosine law for emission from the filament. Pyrometers have long been designed under the restrictions of angular aperture arising from experiments of Fairchild and Hoover (1912) and of Worthing and Forsythe (1914) suggested to minimize the filament fringes.

Cunnold<sup>6</sup> has suggested that as long as the ratio of filament brightness to background brightness is constant it need not be 1. Tests by various observers of a radiation pyrometer in which an iris diaphragm varied the exit aperture from 0.02 to 0.07 radian showed that as the aperture increased the filament disappearance became less perfect but that the accuracy of temperature readings increased. Increasing the light in a pyrometer is advantageous for it permits the use of more-nearly monochromatic filters and permits extension of the optical scale to lower temperatures.

A method of contrast may be used in reading an optical pyrometer to increase slightly the precision and to decrease eye fatigue. A piece of clear glass is held in front of the objective and the current adjusted so that the filament is seen as slightly brighter than the background. When the glass is removed the filament appears slightly darker than the background. By successive trials an equality of contrast is attained. The same result may be accomplished by introducing in the filament circuit a small resistor which can be momentarily short-circuited to produce contrast in filament brightness.

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<sup>6</sup> F. A. Cunnold, *Proc. Roy. Soc.* 152A, 64 (1935).

### Calibration

The primary calibration of an optical pyrometer is made at the temperature of solidifying platinum (1773°C.). A closed-end porcelain tube immersed in the platinum serves as a glowing blackbody target. A precision laboratory optical pyrometer is used to calibrate service pyrometers without necessarily using a blackbody. The comparison usually is made with the aid of a broad-filament tungsten lamp, which may draw 15–20 amp. at 6 v. If a curve of filament current vs. temperature is constructed for the comparison lamp, it may be used as a pyrometer scale. This is an especially convenient procedure for comparing standards in different laboratories.

Pyrometers which have milliammeters as their indicating instruments require a calibration curve or table for converting milliampere readings into temperatures. A three-term interpolation equation can be used over a wide range of temperatures,

$$i = a + bt + ct^2 \quad (6)$$

### Precision and accuracy of partial radiation pyrometers

The precision of most portable partial radiation pyrometers is limited by the milliammeter. In a self-contained pyrometer the balance of the delicate milliammeter mechanism is likely to be affected by different orientations of the instrument. Its scale is necessarily too short to define the value of the current with precision. Measurements are not made with the filament current below a certain minimum value, about 0.2 amp., corresponding to 800°C. With an ordinary milliammeter only about half the scale is then useful. A milliammeter can be calibrated with a depressed zero, but this has the disadvantage of a constant tension on the spiral spring resulting in gradual displacement of the zero. It is preferable, when possible, to use the milliammeter as a

null instrument in a Wheatstone bridge or potentiometer circuit. An empirical expression given by Ribaud for determining the temperature variation  $\Delta T$  corresponding to a current variation  $\Delta i$  is

$$\frac{\Delta i}{i} = 1.9 \frac{\Delta T}{T} \quad (7)$$

Hence to have an uncertainty of only  $1^\circ$  at  $2000^\circ\text{K}$ . the current must be known within an uncertainty of  $1/1000$ . A precision of 1 part in 3000 has been attained in optical pyrometers. This requires a current constant to 0.01%.

The most common cause of inaccuracy in temperatures determined with an optical pyrometer is the uncertain value of the emissivity  $e_\lambda$  of the surface of the test body. An optical pyrometer is calibrated to read blackbody temperatures. If it is sighted upon a surface whose emissivity is not unity it indicates a temperature lower than the true temperature. If the emissivity of the surface is known an appropriate correction can be made to the pyrometer reading. If the true temperature is obtained independently (by a thermocouple) the emissivity of the surface can be calculated for use in making subsequent measurements with an optical pyrometer.

By Wien's law,

$$J_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$$

For a non-blackbody at the same absolute temperature but at blackbody (apparent) temperature  $T_a$

$$J'_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T_a}}$$

from which

$$e_\lambda = \frac{J'_\lambda}{J_\lambda} = e^{\frac{c_2}{\lambda} \left\{ \frac{1}{T} - \frac{1}{T_a} \right\}}$$

or

$$\log_e e_\lambda = \frac{c_2}{\lambda} \left\{ \frac{1}{T} - \frac{1}{T_a} \right\} \quad (8)$$

A pyrometer lamp suffers a slow change in calibration during use owing to gradual evaporation of its filament. A lamp which has been aged for 24 hr. at about 2200°C. before standardization will maintain its calibration within 1° for hundreds of hours of subsequent use at temperatures which do not exceed 1400°C. It is desirable to have at least one spare lamp with each pyrometer which can be used exclusively for checking and if necessary recalibrating the service lamp.

### Summary

A total radiation pyrometer measures the temperature of a test body in terms of its radiation, according to the Stefan-Boltzmann law:  $W = \sigma AT^4$ . The sensitive element is a thermocouple and the measuring instrument is a galvanometer or potentiometer. Calibration for blackbody conditions is made by using radiation from a cavity of known temperature. The range of the pyrometer may be increased by decreasing its aperture from  $A_1$  to  $A_2$  when, for a given galvanometer deflection,  $A_1/A_2 = T_2^4/T_1^4$ . In practical use error arises from the fact that the emissivity of the test body usually is not unity. If its value is known the pyrometer indication  $T_a$  can be corrected:  $T = (T_a^4/\epsilon_t)^{1/4}$ . Otherwise the use of a closed-end tube as a target aids in approximating the blackbody conditions for which the pyrometer was calibrated.

Optical (partial radiation) pyrometers utilize Wien's law  $J_\lambda = Ac_1\lambda^{-5}e^{-\frac{c_2}{\lambda T}}$  to measure the temperature of a test body by comparing monochromatic radiation from it with that of a calibrated filament. The measuring instrument is usually a galvanometer or potentiometer. Its range may be extended by use of a filter of absorption coefficient  $k$ :

$$\frac{1}{T} - \frac{1}{T_a} = \frac{-k\lambda x}{c_2}.$$

When used under non-blackbody conditions optical pyrom-

eter indications must be corrected by an amount depending on the emissivity:

$$\log_e e_\lambda = \frac{c_2}{\lambda} \left\{ \frac{1}{T} - \frac{1}{T_a} \right\}$$

A color pyrometer is designed to measure the temperature of objects whose emissivities are unknown but which approximate a gray body, i.e.,  $e_\lambda = e_\lambda''$ .

Optical and radiation pyrometer readings are independent of distance subject to the conditions already discussed. Both are affected by absorbing media to an extent indicated by combining the equation for absorption with the Wien or Stefan-Boltzmann law respectively. There is no upper limit to the temperatures which can be measured by such pyrometers. The lower limit, in practice, is about 110°C., depending on the particular design of instrument.

## References

- "VI Report on the Heterogeneity of Steel Ingots," *Iron Steel Inst. Spec. Rept.* No. 9, 1935. 236 pp.
- Judd, D. B. "Changes in Color Temperature of Tungsten-filament Lamps at Constant Voltage," *Nat. Bur. Standards J. Research* 17, 679-695 (1936).
- Wensel, H. T., Judd, D. B., and Roeser, W. F. "Establishment of a Scale of Color Temperature," *Bur. Standards J. Research* 12, 527-536 (1934).

## Problems

1. A radiation pyrometer indicator gives full-scale deflection for 1400°F. What fraction of the pyrometer aperture should be diaphragmed to make the same deflection correspond to 2100°F.?
2. A radiation pyrometer sighted on clean, melting copper reads 1970°F. Find the per cent error in its calibration.
3. A radiation pyrometer sighted on the surface of molten metal indicates the temperature 1100°C. while a standard thermocouple gives the temperature as 1210°C. What is the emissivity of the surface?
4. A dusty radiation pyrometer mirror has a coefficient of reflection of 95 per cent of the value for which the instrument was calibrated. If the pyrometer indicates 1600°C., what is the true temperature?

5. Calculate the length of porcelain tube of inside diameter 5 cm. and emissivity 0.5 which must be immersed in molten metal to serve as a 99 per cent "black" source for pyrometer measurements.
6. The tube of Prob. 5 is mounted in a furnace wall 10 cm. thick. What is the maximum distance at which a radiation pyrometer may be sighted on it, if the instrument requires a ratio of source diameter to source distance of 1:8?
7. A radiation pyrometer is sighted through a "gray" window of absorption coefficient  $\mu$  and thickness  $x$  on the surface of a molten metal which has a total emissivity  $e$ . Derive the relation between the true temperature of the metal  $T_t$  and the temperature indicated on the pyrometer  $T_a$ .
8. An optical pyrometer receiving radiation from the inside of a hollow metal wedge indicates the temperature 1400°C. When sighted on the outer surface it indicates the temperature 1270°C. What is the emissivity of the metal?
9. What thickness of glass of absorption coefficient 0.1 mm.<sup>-1</sup> is needed to change the maximum reading of a Morse optical pyrometer from 1500°C. to 2000°C.? Where should the filter be placed?
10. Show, with the aid of a diagram, that ideally the readings of an optical pyrometer are independent of distance. What practical restrictions are there on this statement?
11. A certain optical pyrometer has an objective lens of focal length 10 inches. What provision should be made for change of focus if the sighting distance varies from 1 to 25 feet?
12. An optical pyrometer sighted on a furnace through a glass window indicates a temperature of 1200°C. If an additional window similar to the first is placed in the light path the temperature indicated is 1100°C. Find the true temperature.
13. What is the effective absorption coefficient of the glass windows in Prob. 12 if each had a thickness of 1.5 mm.?
14. An optical pyrometer is sighted through a window of absorption coefficient  $\mu$  and thickness  $t$  on the surface of a molten metal which has emissivity  $E_\lambda$ . Derive the relation between the true temperature of the metal  $T_t$  and the temperature indicated by the optical pyrometer  $T_a$ .
15. If the blackbody temperature of molten iron is 2400°F., what is its color temperature?
16. The uncertainty in obtaining the visual match in an optical pyrometer is approximately 0.002. Find the corresponding uncertainty in temperature measurements at 1000°, 2000°, and 4000°C.

## Resistance Thermometry

## Introduction

The electrical resistance of pure metallic conductors varies with the temperature. This change in resistance is rather large, being 39% for platinum between  $0^{\circ}$  and  $100^{\circ}\text{C}$ . Resistance measurements can be made with high precision. These facts suggest that it should be possible to measure temperature and temperature differences accurately in terms of the resistance of a wire of pure metal provided the relation between resistance and temperature can be found.

Resistance thermometers were suggested by Siemens<sup>1</sup> in 1871 and were quickly adopted for industrial measurements. However the Siemens resistance thermometer, in which the wire was wound on a clay cylinder and enclosed in a wrought iron tube, was not satisfactory for use at high temperature owing to contamination of the platinum which destroyed the reproducibility of the measurements. The precision and reliability of modern resistance thermometers began with the work of Callendar<sup>2</sup> who devised methods of protecting the platinum coil from chemical alteration and showed that its measurements were then reproducible when compared with a gas thermometer.

Platinum resistance thermometers are used over the wide range from  $-259^{\circ}$  to  $1100^{\circ}\text{C}$ . with uncertainties of the order of  $0.04^{\circ}$  to  $0.3^{\circ}\text{C}$ . at low and high temperatures in this range. Phosphor bronze resistance thermometers are used to indicate temperatures as low as  $1^{\circ}\text{K}$ .

<sup>1</sup> K. W. Siemens, *Proc. Roy. Soc. (London)*, 19, 443 (1871).

<sup>2</sup> H. L. Callendar, *Phil. Trans. (Lond.)*, 178, 160 (1887); *Phil. Mag.*, 32, 104 (1891).

Platinum is an especially suitable material for resistance thermometry because of its stability and the simplicity of its resistance—temperature relation. Copper resistance thermometers are suitable for the measurement of moderate temperatures, usually below 100°C. Copper has the advantage of a resistance-temperature relation which is nearly linear, but has the disadvantage of low resistivity. Nickel is an inexpensive substitute for platinum for resistance measurements below 300°C.

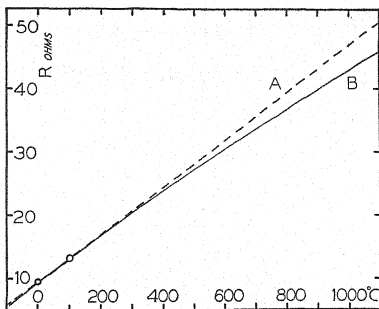


FIG. 65.—(A)  $R_t = R_0(1 + A_0t)$ . (B)  $R_t = R_0(1 + At + Bt^2)$ .

### Resistance-temperature relation

If the resistance of a platinum thermometer varied directly as the temperature it could be represented by line *A* in Fig. 65. Actually the relation is not linear and it is found necessary to use a second degree equation to express the resistance  $R_t$  at a given temperature  $t$  in terms of the resistance  $R_0$  at 0°C.,

$$R_t = R_0(1 + At + Bt^2) \quad (1)$$

This equation is represented by curve *B* in Fig. 65. Callendar devised a method for using this relation in practical measure-



ments and introduced a nomenclature which has come into common use. To avoid solving the quadratic equation directly it is convenient to assume a relation of the form

$$R_t = R_0(1 + A_0 pt) \quad (2)$$

where  $A_0$  is the mean temperature coefficient of resistance between  $0^\circ$  and  $100^\circ\text{C}$ . The temperature determined from Eq. 2 is nearly equal to the true temperature  $t$ , and is called the platinum temperature. It is defined by

$$pt = \frac{R_t - R_0}{R_{100} - R_0} 100 \quad (3)$$

in which  $R_t$ ,  $R_0$  and  $R_{100}$  denote the resistance at  $t^\circ$ ,  $0^\circ$  and  $100^\circ\text{C}$ ., respectively. The difference between the true temperature  $t$  and the platinum temperature  $pt$  is given by the formula

$$t - pt = \delta \left\{ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right\} = d(t - 100)t$$

It will be observed that this is equivalent to the formula

$$t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left( \frac{t}{100} - 1 \right) \frac{t}{100} \quad (4)$$

which is the original form of Callendar's equation.  $\delta$  is a constant characteristic of the individual thermometer to be determined by calibration of the thermometer at some fixed point, preferably the boiling point of sulfur.

In describing a thermometer, the quantity  $R_{100} - R_0$  is called the fundamental interval. The mean value of the temperature coefficient of resistance between  $0^\circ$  and  $100^\circ\text{C}$ .,  $c = (R_{100} - R_0)/100R_0$ , is called the fundamental coefficient.

Equation 4 may be regarded as the fundamental, empirical equation for platinum resistance thermometry. A relation between it and Eq. 1 may be shown as follows,

$$\begin{aligned}
 t - pt &= t - \frac{R_t - R_0}{R_{100} - R_0} 100 \\
 &= t - \frac{At + Bt^2}{100A + (100)^2 B} 100, \text{ from Eq. 1} \\
 &= - \frac{(100)^2 b}{A + 100B} \left\{ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right\}
 \end{aligned}$$

Thus Callendar's constant  $\delta$  in Eq. 4 is equal to  $-(100)^2 B / (A + 100B)$  and  $d = 10^{-4}\delta$ . The value of  $\delta$  for platinum wires is between 1.49 and 1.50. The higher the purity the greater is  $A$ .

The difference coefficient  $d$  must be separately determined for each thermometer. In order that the solution of a quadratic equation for each temperature may be avoided it is convenient in practice to compile a table showing values of the correction  $X$  which must be added to the platinum temperature to give the correct temperature. Such a table<sup>3</sup> constructed for a given value of  $d$  can be used to calculate the correction  $X'$  for another thermometer having a difference coefficient  $d'$  by,

$$X' = \frac{d'}{d} X \quad (5)$$

For convenience in making calculations with a computing machine, Eq. 1 may be put in the form

$$\frac{R_t - R_0}{R_0} = t(A + Bt) \quad (6)$$

The three constants in the Callendar calibration equation for a platinum resistance thermometer are determined from resistance measurements at three temperatures, usually 0°, 100° and 444.6°C. The calibration may be extrapolated to at least 1000°C. and gives results in excellent agreement with the thermodynamic temperature scale. However the

<sup>3</sup> G. S. Callendar and F. E. Hoare, *Correction Tables for Use with Platinum Resistance Thermometers*, London: E. Arnold & Co., 1933.

Callendar equation is not general in its applicability to metallic resistance thermometers. It is not valid for the other common resistance thermometer materials, copper and nickel, or for alloys or even for metals of the platinum group such as palladium.

### Resistance thermometer construction

In preparing a platinum resistance thermometer, platinum wire is doubled on itself (to avoid inductive effects) and then wound on a frame of thin, serrated mica. The ideal mounting is one that leaves the wire as free as possible from mechanical constraints, so that the dimensional changes resulting from

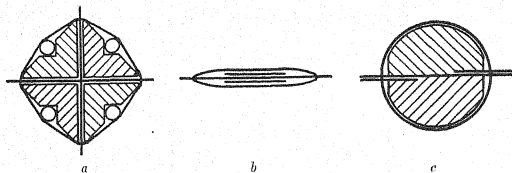


FIG. 66a, b, and c.—Types of resistance thermometer windings in cross section.

thermal expansion shall impose a minimum of mechanical stress on the platinum. Other requirements are that the mounting shall be such that the thermometer will not have excessive time lag, and that the heating effect of the measuring current shall not be excessive. The platinum must not be in contact with materials which may contaminate it.

A great deal of ingenuity has been expended in modifying Callendar's basic mica-cross design so as to reduce the tendency to strain the wire. The modifications have consisted essentially in winding the wire so that the individual turns are circular in form rather than square, and pass through holes or slots in the mica rather than being wound into notches. With this construction (Fig. 66a) the wire is permitted a small amount of motion relative to the mica, but the possible motion is limited so that the coil retains its shape.

The mica cross is held in a quartered mandrel (shown shaded). A small glass capillary tube is laid in each of the four grooves of the mandrel and the platinum wire wound around the form. The capillaries are then removed and the wire pressed against the face of the mandrel, which forces the wire away from the mica grooves and minimizes possible strain. The mandrel is finally removed, leaving a coil similar in appearance to that of Fig. 67 (for which the platinum wire was first coiled in a tiny spiral before being wound on the mica form).

The calorimetric type of thermometer is wound on a flat mica support designed to attain thermal equilibrium with its surroundings rapidly. The two mica strips shown in Fig. 66*b* serve the same purpose as the glass capillaries and are removed after the winding is completed.

Another strain-free type of support consists of a mica strip and two smaller mica spacers. Winding is done on a circular mandrel (Fig. 66*c*), the mica being threaded through holes in the mica. When completed the mandrel is removed and the spacers moved through 90°.

After being wound on its supporting frame, the platinum wire is annealed to relieve strains and insure the reproducibility of later resistance readings. The annealing is sometimes done by "flashing" the filament at about 600°C., or the wire may be repeatedly heated to about 480°C. and cooled in liquid air<sup>4,5</sup>. The annealing temperature should be above the maximum to which the thermometer will be subjected in measuring temperatures.

Protecting casings for resistance thermometers are made of pyrex glass, fused quartz, nickel or porcelain, with or



FIG. 67.—  
Mica-cross  
potential-terminal type  
resistance thermometer.  
(Leeds &  
Northrup Co.)

<sup>4</sup> B. Brenner, *Ind. Eng. Chem.*, 27, 438 (1935).

<sup>5</sup> J. J. Manley, *Phil. Mag.*, 23, 695 Supp. (1937).

without an additional outer jacket of iron or chromel. The thermometer case may be filled with dry air under a pressure of  $\frac{1}{3}$  to  $\frac{1}{2}$  atm. at room temperature. The oxidizing atmosphere is an advantage.

For the connecting wires inside the protection tube, gold has been found very satisfactory. It is cheap, easily worked,

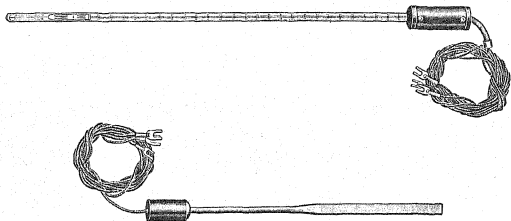


FIG. 68.—Platinum resistance thermometers. (*Leeds & Northrup Co.*)

inert, of suitable resistivity, and has a low thermoelectric power against copper. The lead wires from the protecting enclosure to the measuring instrument may be single copper wires of appropriate size, say, No. 26 gage.

Figure 68 illustrates two laboratory-type resistance thermometers, one in a Pyrex protecting tube, the other in a

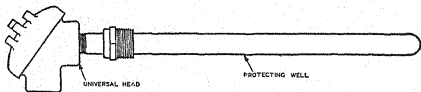


FIG. 69.—Industrial resistance thermometer. (*Leeds & Northrup Co.*)

sheath of copper-nickel alloy. The external appearance of an industrial-type resistance thermometer is indicated by Fig. 69.

The characteristics of thirteen types of resistance thermometers were investigated by Manley.<sup>5</sup> Table I is a partial

summary of his findings. In columns 7 and 8 are given the times required for the thermometer to cool  $1/e$  of the difference from  $23^{\circ}$  to  $20^{\circ}\text{C.}$  in air within a black chamber and in water, respectively. These values are a measure of the thermometer's temperature lag. In the last column sensitivities are listed relative to an arbitrary standard.

TABLE I  
RESISTANCE THERMOMETER CHARACTERISTICS<sup>5</sup>

Thermometer	Bulb, containing length diameter tube			Diameter wire	$R_0$	Time to cool $1/e$ of difference $23^{\circ}$ to $20^{\circ}\text{C.}$		Sensitivity relative to standard
						In air	In water	
4 spirals.....	Fused silica	34 mm.	7.5 mm.	0.05 mm.	54.11	62 sec.	3.0 sec.	20.8
Wire embedded in fused silica.....	Fused silica	28	3.2	.04	25.00	88	1.2	9.6
Spiral on mica plate.....	Glass	Flat bulb $26 \times 7 \times 2 \text{ mm.}$		.05	22.88	30	2.9	8.8
Twin spirals.....	Fused silica	35	6.5	.05	19.49	55	3.2	7.5
Single spiral.....	Fused silica	27	5.2	.06	8.59	51	2.5	3.7
Single loop.....	Glass	21	2.2	.025	6.19	34	1.0	2.4
Single loop.....	Glass	38	2.0	.04	5.1	32	1.5	2

### Calibration of a resistance thermometer

The calibration of a resistance thermometer for use above  $0^{\circ}\text{C.}$  requires the determination of the three constants in Eq. 1. This is accomplished by measuring  $R_t$  at the ice, steam and sulphur points, respectively. An ice bath and a hypsometer of the type described under the calibration of thermocouples will do for the first two temperatures. Measurements at the sulphur points are considerably more troublesome.

A form of sulphur-boiling apparatus<sup>6</sup> suited for general laboratory use is illustrated in Fig. 70. The sulphur is held in a pyrex tube wrapped with asbestos paper and surrounded by an iron cylinder and rock wool insulation. The sulphur is boiled by an electric heater made of nichrome wire wrapped around the iron cylinder. The thermometer is inserted into the boiling tube surrounded by a light metallic shield to prevent loss of heat by radiation.

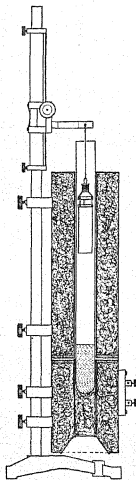


FIG. 70.—Sulphur boiling point apparatus.

A more elaborate form of sulphur-boiling apparatus<sup>7</sup> used in attaining the highest precision of measurement at the sulphur point is shown in Fig. 71. The side arm near the top of the tube leads to a reservoir of inert gas and a manometer, to control and measure the pressure at which boiling occurs. A second heating coil surrounds the upper part of the tube. The current through the lower heater is adjusted so that the sulphur condenses just above the top of the heat jacket. The radiation shield is in the form of two concentric cylinders of aluminum, blackened inside, and provided with a horizontal disk at the bottom to protect the thermometer from splashing. Apparatus of similar design is used to reproduce the boiling points of water and mercury with high accuracy

for calibration purposes.

### Resistance measurements; lead wire compensation

Measurement of the resistance of a resistance thermometer generally is made with some form of Wheatstone network or

<sup>6</sup> C. D. Niven, *Can. J. Research*, 14, 1 (1936).

<sup>7</sup> J. A. Beattie, M. Benedict and B. E. Blaisdell, *Proc. Am. Acad. Arts Sciences*, 71, 327 (1937).

with a potentiometer. The sensitive element of the thermometer is often remote from the measuring device and the connecting wires are subject to varying temperatures along their length. If there were simply two lead wires connecting the platinum coil to the resistance-measuring instrument

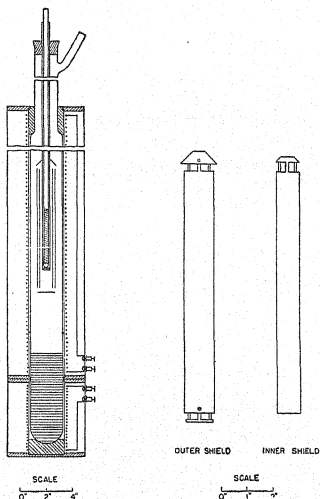


FIG. 71.—Sulphur boiling point apparatus.

the calibration of the thermometer would be indefinite, depending upon the length of lead wire and the depth of immersion of the thermometer. There are three types of resistance thermometer connections commonly used to permit elimination of the effects of the unknown and variable lead wire resistance. These are illustrated in Fig. 72 with the notation suggested by Mueller. Type (a) is used only with



a shunted bridge measuring method. Type (b) is used with either a shunted bridge or a slide-wire bridge. Connections

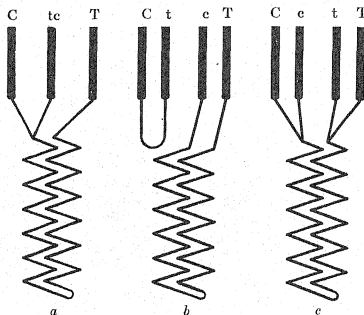


FIG. 72.—Resistance thermometer connections.

of type (c) can be used with a shunted bridge, Kelvin bridge, differential galvanometer or potentiometer measuring method.

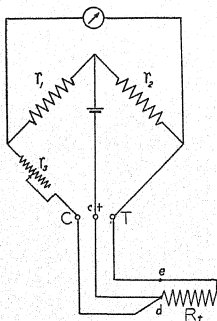


FIG. 73.—Siemen's three-lead compensation.

### Siemens three-lead compensation

The Siemens three-lead compensation method is illustrated in Fig. 73. The lead wires in the thermometer casing are made as nearly as possible the same resistance and the external copper connecting wires must also have equal resistance. From the principle of the balanced Wheatstone network

$$\frac{r_3 - Cd}{r_1} = \frac{R_t - Te}{r_2}$$

If resistance  $Cd$  is constructed equal to  $Te$  and  $r_1$  is made equal to  $r_2$  then  $r_3 = R_t$ .

Hence the measured resistance is independent of lead-wire resistance.

### Callendar four-lead compensation

Callendar's four-lead method is similar to Siemens' method. The platinum coil is connected by a pair of wires to one arm of the Wheatstone network. A second similar pair of wires in the form of a simple loop is placed beside the first pair and connected in the adjacent arm of the network for compensation. A commutator permits interchange of the lead wire pairs.

### Potential terminal compensation

In the potential terminal method of resistance measurement two leads are attached to each end of the thermometer element, Fig. 74. With the commutator in the *N* position the battery is first connected to *c*. When the network is balanced,  $r_3 + Cd = R_t + Te$ . By rotating the commutator the battery is then connected to terminal *t* and the terminals *T* and *C* are interchanged. Then for balance

$$r_3' + Te = R_t + Cd$$

On combining these two equations we obtain

$$R_t = \frac{r_3 + r_3'}{2}$$

Thus the measured resistance of the thermometer coil is

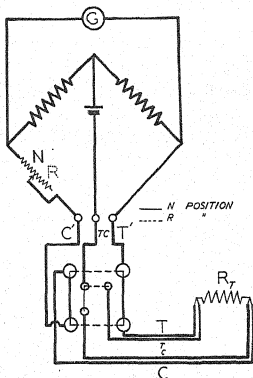


FIG. 74.—Potential terminal method, using Mueller bridge and commutator.

independent of the resistances of the lead wires. Any error which might result in either of the previous methods owing to unequal lead wire resistance is eliminated in the potential terminal method.

### Potentiometer method

The resistance of a four-lead thermometer can be determined with a potentiometer (Fig. 75). The current, adjusted to a suitable value by resistor  $r_1$ , flows through the ther-

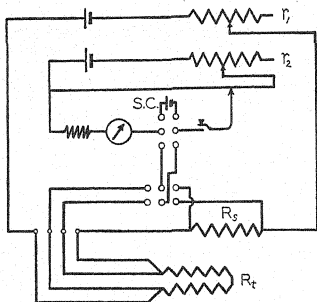


FIG. 75.—Potentiometer method.

mometer coil and through a standard resistor  $R_s$ . The potential drops  $e'$  and  $e$  across  $R_s$  and  $R_t$  respectively are measured by the potentiometer. The resistance  $R_t$  is determined from the relation  $R_t = R_s \frac{e}{e'}$ . If the resistor  $R_s$  is a variable one it may be adjusted to make  $e = e'$  and its dial calibrated to give  $R_s = R_t$  directly. Measurements with a potentiometer are independent of lead wire resistance.

Since  $dR/dt$  is about 0.004 in the neighborhood of  $0^\circ\text{C}$ . in order to measure temperature to within  $0.01^\circ\text{C}$ . the resistance must be determined with a relative error less than 0.00001. For a thermometer having  $R_0 = 10$  ohms and using

a current of 0.00004 amp. this relative error corresponds to an error of 0.4 microvolt in the potentiometer measurement. Parasitic thermal e.m.f.'s produced in the measuring circuit make it difficult to attain such accuracy. This suggests the advantage of using thermometers of relatively large resistance and measuring currents sufficiently large so that the e.m.f.'s to be measured are of the order of 0.05 volts. A potentiometer of proper design used with precautions permits temperature measurements to within  $0.01^{\circ}\text{C}$ .

### High precision Wheatstone networks

Resistance thermometers are designed usually to have a resistance between 2.5 and 25 ohms at  $0^{\circ}\text{C}$ . Measurements of temperatures to  $0.01^{\circ}\text{C}$ . with a 25-ohm thermometer require that resistance measurements be accurate to 0.001 ohm. A conventional Wheatstone network represented in the preceding figures has the variable resistance of its contacts placed directly in the bridge arms. Any variation in the resistances of the slide or plug contacts affects the balance of the network and may be of the same order of magnitude as the change in the thermometer resistance which it is desired to measure. Another handicap of such a bridge is that the resistance of the network and hence of the galvanometer circuit varies with the value of the resistance being measured. This upsets the galvanometer damping.

A consideration of the diagram in Fig. 76, in which  $r_1$  and  $r_2$  are the equal ratio arms shows that resistance may be transferred to or from the other arms in three ways: (i) by moving  $D$  along  $BDC$ , (ii) by moving  $B$  along  $DBG$ , and (iii) by moving  $C$  along  $DCG$ . The first method is essentially that used in the Callendar-Griffiths bridges. In it the network balance is independent of possible variations in the resistances of the movable contact. In methods (ii) and (iii) the effect of variable contact resistance may be reduced to any desired extent by increasing  $r_1$  and  $r_2$  with which the contacts are in series.

In practice the adjustable resistance of a network designed for temperature measurement is in the form of dial decade units. There is a variety of types of adjustable resistance elements used in precision resistance networks.<sup>8</sup> In the commonest type, the effect of contact resistance is minimized by shunting the variable resistance with a relatively low-valued resistor. Such an arrangement is shown in the circuit of Fig. 114, Chap. X. A moderate precision bridge is illustrated

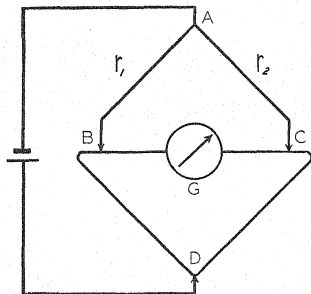


Fig. 76.—Simple Wheatstone bridge.

in Fig. 77 connected to a three-lead type resistance thermometer for laboratory measurements. Figure 78 shows an indicator for permanent installation. This has a self-contained rotary selector switch for successive measurements on several thermometers.

### Practical applications of resistance thermometers

In the measurement of extreme temperatures the importance of resistance thermometers for industrial measurements is limited by their fragility and the numerous precautions necessary for accuracy. In the range of moderate temperatures, however, resistance thermometers have many

<sup>8</sup> E. F. Mueller and F. Wenner, *J. Research Nat. Bur. Standards*, 15, 477 (1935).

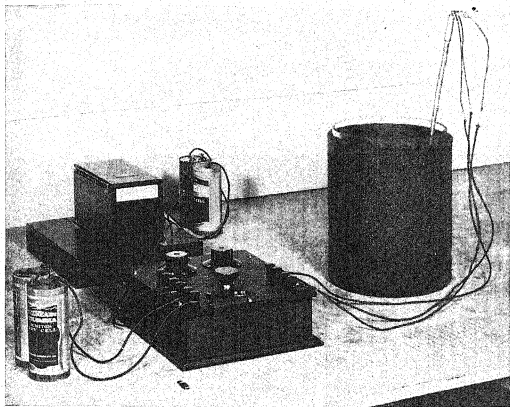


FIG. 77.—Bridge for resistance thermometer measurements of moderate precision.  
(Leeds & Northrup Co.)

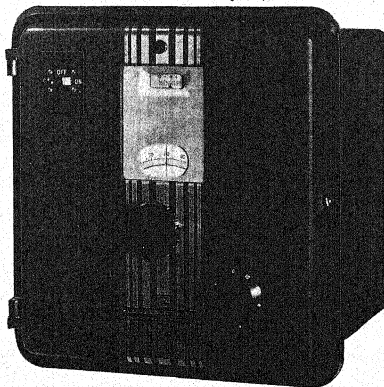


FIG. 78.—Panel indicator for resistance thermometers. (Leeds & Northrup Co.)

applications, particularly where high inherent accuracy or ability to handle extremely short ranges is important. A resistance thermometer is particularly useful when small temperature changes must be measured or when the average temperature of a small region is desired. A resistance thermometer is free from reference junction annoyances characteristic of thermocouples.

In one form of resistance thermometer platinum wire is fused in glass for support and protection.<sup>9</sup> Measurements up to 550°C. are made with an accuracy of +0.15%, which is superior to that obtained with a thermocouple.

In comparison with resistance thermometers, thermocouples are, in general, simpler—easier to make, easier to inspect, easier to maintain. Usually cheaper to buy, they are generally preferred wherever they meet the requirements of a given application for range, sensitivity, accuracy, etc. In addition the use of couples is sometimes dictated by space requirements.

For practical applications the Wheatstone network used with a resistance thermometer need not be used as a null instrument, which requires manual adjustments for each reading, but it can be used as a deflection (unbalanced) bridge for which the galvanometer deflection is calibrated to indicate directly the temperature of the sensitive coil. Resistance thermometers are an important form of remote-indicating instrument used for aircraft temperature measurements. The somewhat variable voltage of the usual 12 v. battery necessitates the use of a voltage regulator. A deflection-type bridge is used. A selector switch permits reading any one of a number of thermometer coils on a single indicator. Figure 79 shows how such an installation may be modified for operation on alternating current with the addition of a transformer and a copper-oxide type rectifier *C* to the voltage regulator *V* and bridge circuit *W*.

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<sup>9</sup> W. Goedecke, *Electrowärme*, 4, 278 (1934).

A bolometer<sup>10</sup> is a resistance thermometer made of thin foil which has small thermal capacity and very great sensitivity. With it, changes in temperature as small as  $0.000001^{\circ}\text{C}$ . can be detected, permitting relative measurement of the distribution of energy in the spectrum of a laboratory light source or of a distant star. Bolometers are used in direction finding by infra-red rays.<sup>11</sup>

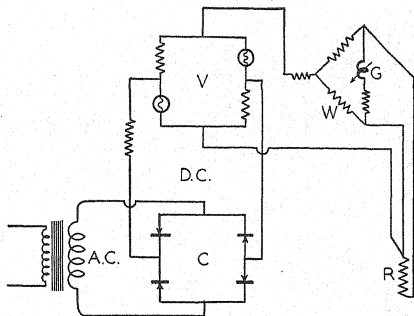


FIG. 79.—Operation of resistance thermometer from a.c. supply. (Lewis Engineering Co.)

Electric power plants depend on temperature measuring equipment for protection against overheating and for determining maximum safe loading. To prevent overheating of generators, frequency changers, synchronous condensers and large motors an automatic recorder and alarm is desirable. Detectors may be either thermocouples or resistance thermometers. Some power plant temperature equipment requires special design. For example, since thermocouple and resistance thermometers are not suitable for installation in a rotating field, the resistance of the field winding itself is

<sup>10</sup> S. P. Langley, *Am. J. Science*, 21, 187 (1881).

O. R. Lummer and F. Kurlbaum, *Ann. Physik*, 46, 204 (1892).

<sup>11</sup> G. Gresky, *Z. Instrumentenk.*, 52, 255 (1932).



measured. This varies with the temperature and serves as an index of that temperature. Because the resistance of the winding is too low for accurate measurement with a Wheatstone bridge, the Kelvin bridge is employed.

Figure 80 represents schematically the elements of a Kelvin bridge circuit. The lead  $d$  connects the field winding  $X$  and a low-resistance standard shunt  $R$  in series in the d-c. field supply circuit. Brush contacts on the collector rings, representing potential points at the terminals of the field winding, are connected to potential posts on the shunt, through the fixed resistances  $B$ ,  $A$  and  $b$ ,  $a$ , with a slidewire

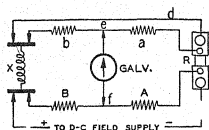


FIG. 80.—Kelvin bridge circuit (simplified). (*Leeds & Northrup Co.*)

resistance between  $B$  and  $A$  and another between  $b$  and  $a$ . The terminals of the galvanometer are connected to the contacts  $e$  and  $f$  on these slidewires. A condition of electrical balance is established by adjusting these contacts until galvanometer deflection is reduced to zero. Resistances are then in

the relation:  $X/R = B/A = b/a$ .

## Summary

Temperature can be measured in terms of the electrical resistance of a metallic conductor, usually platinum, nickel or copper. Platinum resistance thermometers are used over the range  $-259^{\circ}$  to  $1100^{\circ}\text{C}.$ , and provide the most accurate method of measurement in the range of medium temperature. The reproducibility of the scale of a resistance thermometer depends on the purity and homogeneity of the resistance element and its protection from strain and contamination. Boiling point apparatus used in the calibration of a resistance thermometer must provide for adequate depth of immersion and radiation shielding. An accurate manometer is an essential part of the calibrating apparatus. Electrical measurements are best made with a Wheatstone bridge or potentiometer so constructed as to minimize the

effect of contact resistance and e.m.f. and to eliminate the effect of the resistance of the thermometer lead wires.

### Problems

1. A platinum resistance thermometer has the following resistances: 11.00 ohms at  $0^{\circ}\text{C}.$ ; 15.247 ohms at  $100^{\circ}\text{C}.$ ; 28.887 ohms at  $444.60^{\circ}\text{C}.$  Find the numerical value of  $\delta$  in the Callendar correction formula.
2. At what temperature would the resistance of this thermometer (Prob. 1) become zero assuming the same equation held at low temperature? What is found experimentally?
3. What are the merits and disadvantages of deflection-type (i.e., unbalanced) Wheatstone bridges used in temperature measurements?
4. In a Wheatstone bridge,  $r_1 = r_2 = 1000$  ohms. At  $0^{\circ}\text{C}.$   $r_3 = r_4 = 10$  ohms. What should be the smallest graduation of resistance  $r_3$  and the current sensitivity of the galvanometer (coil resistance = 1000 ohms) in order to detect a change in temperature of  $0.1^{\circ}\text{C}.$ ?
5. What difference of potential will be produced at the galvanometer in Prob. 4 if the temperature of the resistance bulb is raised to  $100^{\circ}\text{C}.$ ?
6. Consider two platinum thermometers at the same platinum temperature. Let

$$X = t - pt = d(t - 100)t,$$

$$X' = t' - pt' = d'(t' - 100)t',$$

and

$$t' = t + x, \quad \text{and} \quad d' = d + y.$$

Show that for  $x \ll 2t - 100$

$$x = \frac{yX}{d\{1 - d'(2t - 100)\}}$$

If correction tables are available for a particular thermometer show how they may be applied to any other thermometer using this equation. (Reference 3.)

7. Diagram a circuit in which the heating coil of a small platinum-wound furnace is used as a platinum resistance thermometer to measure its temperature.
8. It is desired to make a nickel resistance thermometer which will have a resistance of 10 ohms at  $0^{\circ}\text{C}.$  What length of wire of diameter 0.0031 inch (B. & S. No. 40) and of resistivity 50 ohms per circular mill-foot at  $68^{\circ}\text{F}.$  should be used for the thermometer coil? What will be its resistance at the normal boiling point of water? Of naphthalene?
9. Draw a diagram of a resistance thermometer connected to a Callendar and Griffiths bridge and explain how measurements are made. (Consult general references of Chap. I.)

## Recording Pyrometry

### Introduction

Permanent temperature records are of primary importance in every industrial process and laboratory research whose results are dependent upon the maintenance of certain optimum temperatures. The pyrometers that can be made to record automatically are of the following classes: (i) expansion thermometers, using a gas, liquid, or solid in the sensitive element; (ii) resistance thermometers; (iii) thermoelectric pyrometers; (iv) total radiation pyrometers and (v) partial radiation pyrometers balanced photoelectrically.

Of these types, the thermoelectric pyrometer has the greatest applicability, especially for the higher temperatures at which the first two are not suitable. The constant-volume gas thermometer for industrial use is satisfactory up to about  $400^{\circ}\text{C}.$ , and the mercury thermometer to about  $550^{\circ}\text{C}.$  The resistance thermometer is capable of very high accuracy up to  $1100^{\circ}\text{C}.$  At such high temperatures, however, thermocouples are more serviceable, since deterioration of the wire from repeated heating does not so seriously alter the e.m.f. developed by a couple as it does the resistance of a resistance thermometer. Base-metal thermocouples serve satisfactorily up to  $1100^{\circ}\text{C}.$  and Pt-PtRh couples up to  $1500^{\circ}\text{C}.$ , though above  $1400^{\circ}\text{C}.$  it becomes very difficult to protect the couple from contamination. Radiation pyrometers are useful at the highest attainable temperatures. However, processes in which temperatures greater than  $1600^{\circ}\text{C}.$  are used are not, in general, susceptible of very precise temperature control.

Temperature records are usually kept on disk, drum or strip charts whose temperature-time scales are proportioned to fit the range and accuracy of a particular service. The precision of modern industrial recorders has been improved until a considerable part of the residual error is associated with the effect of humidity changes on the paper charts.<sup>1</sup>

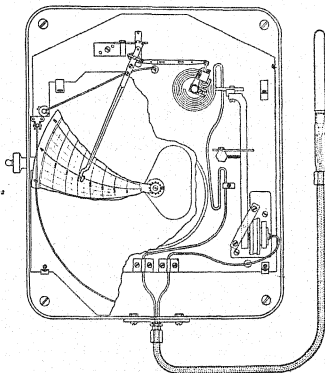


FIG. 81.—Compensated mercury recording thermometer. (C. J. Tagliabue Mfg. Co.)

### Pressure thermometers

Liquid- vapor- and gas-filled thermometer bulbs are used to actuate recording pens through some form of Bourdon tube. When the bulb is remote from the recorder, as is desirable in many installations, it is necessary to compensate for the effect of temperature changes on the pressure-transmitting tube. In the recording mercury thermometer illustrated in Fig. 81, the mercury-filled capillary is paralleled by a casing containing nitrogen. The gas-filled space acts as a

<sup>1</sup> T. R. Harrison, *S.A.E. Journal*, 30, 100 (1932).

long bulb which inflates and deflates a sylphon (capsular spring) inside the recorder case as the temperature fluctuates along the tubing. The sylphon operates through a lever movement to shift the center of the Bourdon spring in the proper sense to compensate for the effect of the varying temperature in the connecting tubing.

In another method of compensation, a fine wire is placed in the capillary bore of the pressure-transmitting tube. By the proper choice of expansion coefficients and dimensions, the expansion of the wire can be made to cancel the effect of the expansion of the capillary tube keeping constant the volume occupied by the liquid.

### **Recording galvanometer**

A galvanometer may be so modified as to become a recording instrument for use with resistance thermometers or thermocouples. A galvanometer suspension is used which permits the galvanometer needle to be depressed by a bar which periodically brings it in contact with a graph sheet. The graph paper is moved at constant speed and the temperature-time curve obtained is a series of closely-spaced dots made by an ink pen, by a stylus on waxed paper or by an electric spark which perforates the paper. An obvious disadvantage of a recording galvanometer is that the weight of the recording mechanism is detrimental to the sensitivity and balance of the galvanometer.

### **Recording potentiometer**

The advantages of the null-indicating principle of a potentiometer are so great in a wide variety of measurements that numerous ingenious methods have been devised to make a potentiometer self-balancing, recording and even automatic in checking itself against a standard cell.

In all recording potentiometers the galvanometer merely indicates the position of balance. It is required to do no work, which would reduce its sensitivity. An electric motor

takes the place of an operator in moving the resistance contacts to secure a balance. A commercial recording potentiometer is an interesting example of a delicate, expensive laboratory instrument which has become a reliable industrial instrument of moderate cost through quantity production.

The balance-type recording mechanism which can apply the potentiometer method for use with thermocouples can

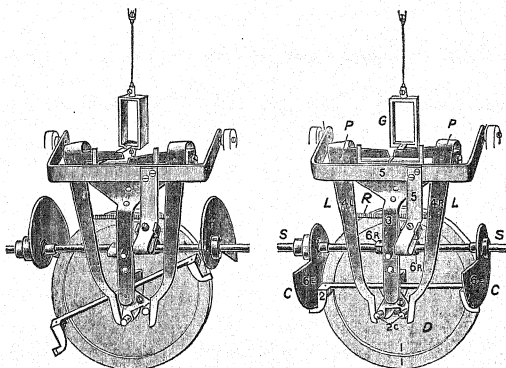


FIG. 82.—Potentiometer balancing mechanism. (*Leeds & Northrup Co.*)

be used equally well to apply the Wheatstone or Kelvin bridge methods for resistance thermometer measurements.

The operation of a self-balancing potentiometer may be well-illustrated by a consideration of one of the older forms of balancing mechanisms, Fig. 82. The slide wire is a long helix mounted on the periphery of the central disk. In balancing, the wire is moved past a stationary contact. Balance is achieved by the following cycle of operations. Suppose the galvanometer *G* is deflected toward the left. Shaft *S* is rotated continually, by a motor not shown. With

each revolution the small cam  $6R$  raises bar 5 which catches the pointer under one of the right-angle levers,  $L$ . This lever, pivoted at  $P$ , is thus made to swing the arm 2 by pressing against one of the eccentrically-located lugs  $2c$ . The rocker arm 5 is then immediately lowered to allow the galvanometer to swing freely. Cam  $6R$  is so fixed on shaft  $S$  that it recedes from spring  $R$  allowing  $R$  to press 2 against the disk  $D$  just before cams  $C$  straighten arm 2. Hence, in so doing, they rotate the disk and the slide wire is brought nearer the position for balance. If balance has not been attained, the galvanometer remains deflected, and the same cycle of operations is carried out with the next revolution of the shaft. When balance is attained, the upward movement of 5 simply raises the pointer into the V-shaped space between levers  $L$ , and no rotation of the disk follows. The position of the slide wire controls the position of a pen carriage on a horizontal rod over the graph sheet. At intervals the pen drops to make a mark on the sheet. The scale of the potentiometer may be graduated in millivolts, or directly in temperature for a given type of thermocouple.

An improved form of balancing mechanism is pictured in Fig. 83. In the original mechanism accuracy was largely limited by mechanical clearances, and these had to be adjusted occasionally owing to wear. In the newer design accuracy and responsiveness are practically unaffected by wear. Deflections of the galvanometer needle as small as 0.001 inch actuates the balancing mechanism. The balancing operations are explained by the illustrations and captions of Fig. 83. The galvanometer has a free period in which to deflect. Then, about once every two seconds, a cushioned clamp grips the pointer and setting levers close on it quickly. If the levers find the pointer undeflected the balancing mechanism and slide wire do not move. If the temperature has changed, the setting levers find the pointer deflected. A clutch arm is positioned to match the extent of pointer deflection, and is clamped there against the slide wire disk.

Cams restore the arm promptly to the normal position, thus simultaneously turning the disk and the slide wire.

The external appearance of a typical recorder is illustrated by Fig. 84. Figure 85 shows the chart holder swung out, exposing the slidewire disk. In Fig. 86 the unit comprising galvanom-

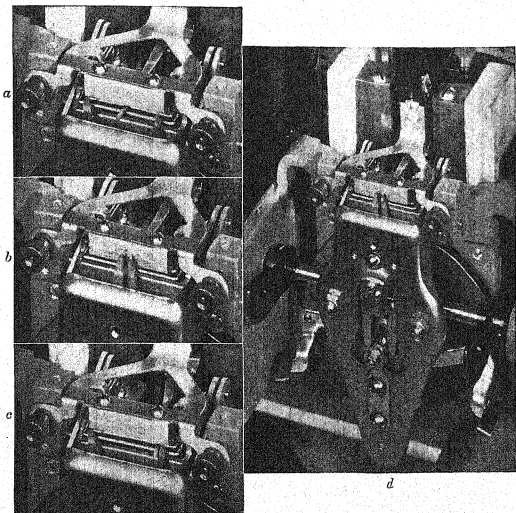


FIG. 83.—Micromax balancing mechanism. (*Leeds & Northrup Co.*)

eter, motor, standardizer and balancing mechanism has been opened. The terminal board, dry cell and motor fuse are exposed on the back wall of the housing.

Such recorders are made in single-point, two-point and multiple-point types. A single-point curve-drawing instrument indicates continuously and traces an uninterrupted record. It concentrates on one couple, is never disconnected



when an important change takes place—especially desirable in a recorder which operates signals. A two-point curve

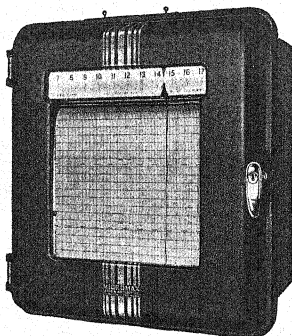


FIG. 84.—Micromax potentiometer indicating recorder. (*Leeds & Northrup Co.*)

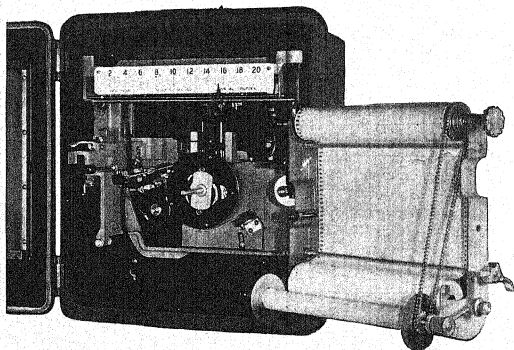


FIG. 85.—Micromax recorder, chart swung out. (*Leeds & Northrup Co.*)

drawing instrument switches automatically from one to the other of two couples at short regular intervals. Its pointer

indicates the two temperatures alternately, and its pen records them side by side for easy comparison. It can be

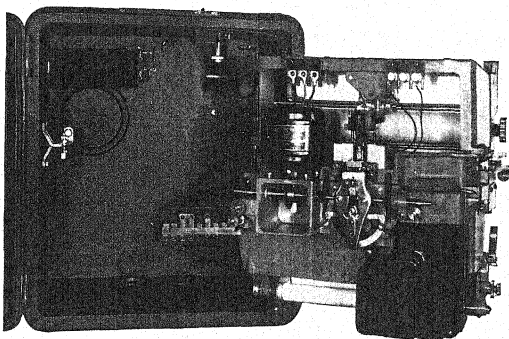


FIG. 86.—Micromax recorder, mechanism swung out. (*Leeds & Northrup Co.*)

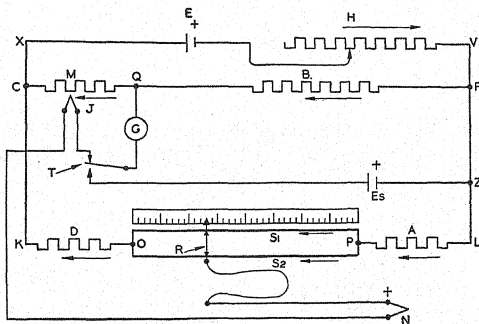


FIG. 87.—Recording potentiometer circuit. (*The Bristol Co.*)

equipped to operate signals. A multiple-point, curve-printing instrument measured successively the temperatures of as many as sixteen couples. It is especially useful where

processes are of long duration, where temperatures tend to change gradually, or where temperatures differ but are always in the same approximate relationship. Its pointer indicates the several temperatures alternately and its printing device records them either in one color or in contrasting

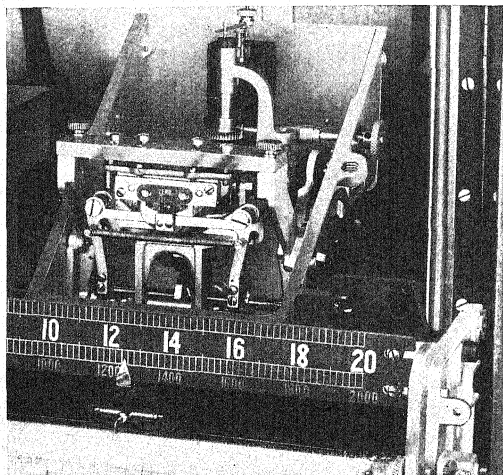


FIG. 88.—Bristol potentiometer recorder. (*The Bristol Co.*)

colors. In addition, it can be equipped to operate (1) a remote indicator, and (2) pilot lights to show at any instant which couple is connected.

A circuit diagram for a recording potentiometer used with a thermocouple is shown in Fig. 87. The balancing mechanism (Fig. 88) adjusts the position of contact  $R$  on the two slide wires,  $S_1$  and  $S_2$ . When the potential difference between  $Q$  and  $R$  has been made zero the galvanometer reads zero, and no further motion of  $R$  takes place. A recording pen

and an indicating arrow mounted on the same carriage as  $R$  show the thermocouple e.m.f. (temperature). Since the e.m.f. of the working battery  $E$  changes slightly from time to time provisions are made whereby the potential difference between  $X$  and  $V$  can be held constant by adjusting the resistor  $H$ . This is done by depressing switch  $T$ , thus temporarily replacing the thermocouple circuit by the circuit

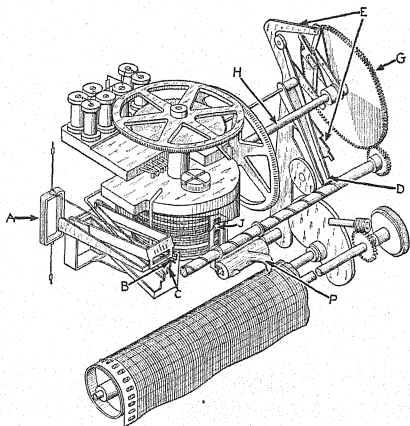


FIG. 89.—Brown potentiometer balancing mechanism. (*The Brown Instrument Co.*)

between  $Z$  and  $T$  of like polarity, containing a standard cell  $E_s$  of constant e.m.f. By adjusting  $H$  until the galvanometer deflection is zero the e.m.f. between  $X$  and  $V$  is restored to its intended value. This operation of standardizing the current through the potentiometer slide wire is done manually on some instruments, automatically on others.

Another type of potentiometer balancing mechanism is shown in Fig. 89. At intervals of a few seconds, the galvanometer pointer  $B$  is lightly clamped. A step on the

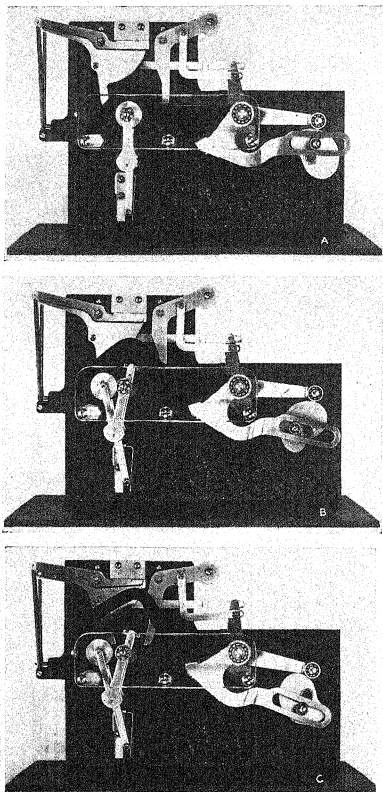


FIG. 90.—Foxboro balancing mechanism (model). (*The Foxboro Co.*)

selector table *C* rests against the pointer and positions a secondary pointer *D*. The step lever *E* periodically moves downward into contact with the secondary pointer and rotates the gear *G*, secured to the shaft *H*, an amount depending upon the position of the secondary pointer. This readjusts the slide wire contact *J*, simultaneously moving the pen *P*.

Still another balancing mechanism is shown in Fig. 90. The two V-shaped sensing fingers detect galvanometer deflections and move a friction roller accordingly. A  $\Lambda$ -shaped drive cam continually moves slowly up and down. In descending it engages a roller and rolls it back to the center of the  $\Lambda$ -shaped cam. As the roller turns, it moves the contact arm along the horizontal, straight slide wire, and a pen along the chart. This method is designed to permit fast movement of the recording device without fast driving of the mechanism, thereby minimizing wear.

### High speed recording

To measure the temperature of metals being rolled, so quickly that even the gradients along their lengths are recorded, a quick-acting radiation pyrometer is used with a rapid recorder. Rapid balancing combined with rapidity of chart movement (of the order of 2 inches per minute) result in clear graphs which permit analysis of even rapid temperature fluctuations.

One such recorder, the Speedomax, has a measuring circuit practically identical with that of the recorder shown in Fig. 84. Instead of balancing by mechanical means, however, the Speedomax has a motor which balances the instrument rapidly whenever a temperature change unbalances the circuit. To assure fast recording, this motor provides higher speeds as temperature changes become larger; big changes record nearly as fast as small ones. To prevent overshooting, an electrical tachometer, built into the motor, reverses motor torque as required for a quick, precise balance.

### Photoelectric recorders

To obtain sensitivity and rapidity of response equal to that of the highest-sensitivity indicating instruments, photoelectric recording is advantageous. Figure 91 shows a photoelectric unit which may be used in conjunction with other instruments to make them recording. For temperature measurements the basic instrument may be a galvanometer

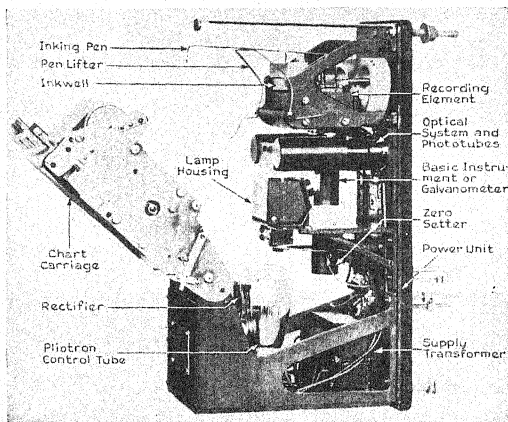


FIG. 91.—Photoelectric recorder. (General Electric Co.)

connected to a thermocouple, a radiation pyrometer or a resistance thermometer bridge circuit. The link between the basic instrument and the recording pen consists of a combined optical system and photoelectric circuit. The basic instrument rotates a mirror, shown in Fig. 92. If this mirror and the one attached to the recording element are parallel, light from a small lamp is reflected equally to each of two photoelectric tubes. No change in the position of the

recording element occurs. If, however, the two mirrors are not parallel, the unbalanced light received by the photo tubes results in a corrective action being applied to the recording pen. Hunting, or oscillation of the mechanism about the position of balance, is presented by a damping resistance and capacity shown in the circuit of Fig. 93.

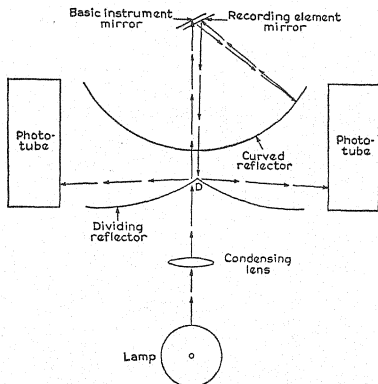


FIG. 92.—Optical system of recorder. (General Electric Co.)

### Special applications

The bulk of temperature recorders is used in metallurgical, chemical and ceramic processes and in power plants. Some of the less-common specialized uses may be suggested. One is a wet- and dry-bulb thermograph for humidity determinations. There are recording clinical thermometers which use a thermocouple or resistance thermometer as the sensitive element. The Callendar sunshine recorder uses a bolometer and a recording Wheatstone bridge.

In checking air conditioning installations a eupathograph records a quantity analogous to the physiological sensation



induced in a human being by a given temperature-humidity environment. The instrument is essentially a hollow blackened copper cylinder, maintained at 75°F., which loses heat to its surroundings at a rate which depends on the conditions.

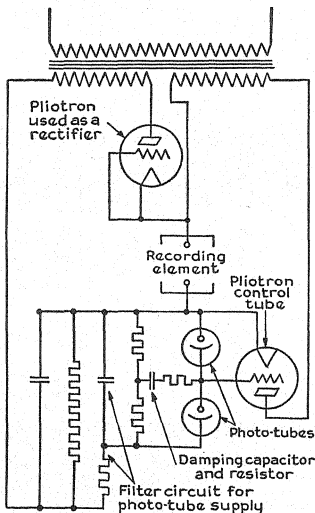


FIG. 93.—Wiring diagram of recorder. (General Electric Co.)

The heat loss is recorded on a scale calibrated in degrees of equivalent temperature.

One form of ship's hold thermometer uses a mercury-in-glass thermometer and photographic recording to provide permanent records for periods up to sixty days duration.

A bottle thermograph can travel on the conveyor used in pasteurizing liquids. It provides a record of the actual

liquid temperature, which may be influenced considerably by the thermal lag of the container.

### Summary

Permanent temperature records are obtained by providing pyrometers of the types already studied (expansion, resistance, thermoelectric and radiation instruments) with mechanical or electrical recording devices. Of the latter the recording potentiometer is especially important both as a laboratory and as an industrial instrument for measuring temperature in terms of an e.m.f. Reliable records are obtained only when the sensitive element is used under conditions for which it was calibrated.

## Automatic Temperature Control

### Introduction

"Have you ever tried to eliminate the fluctuations of temperature in your home? If so, you must have gone through the mental processes required to analyze automatic control problems. You deal with time lags: (a) the time required to build up a draft and a fire, (b) the time required to build up the temperature of the equipment so that heat can be transferred to the air, (c) the time required for the heat to be carried throughout the house and (d) the time required for your thermometer to show this new temperature value. You may not have recognized the various factors to the point where you could separate each one and determine its effect and the way to compensate for it, but you have dealt with the problems which good controllers analyze and solve. . . . The best control system is one that is so well regulated by metered control and so quick to smooth out slight deviations, that it appears to be doing nothing."<sup>1</sup>

Temperature regulation in its crudest form is accomplished by the use of indicating instruments and manual control. Substitution of recording instruments for indicating instruments permits closer manual control by focussing the operator's attention on the importance of time and the rate of change of temperature (both  $\delta T/\delta t$  and  $\delta^2 T/\delta t^2$ ) in correcting for departures of the temperature from the desired value. Completely automatic control of temperature represents one phase of the application of automatic control to industrial processes, which has as its objective the improvement of the

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<sup>1</sup> J. J. Grebe, *Ind. Eng. Chem.*, 29, 1225 (1937).

product and reduction in cost. It often brings, too, a more fundamental knowledge of the process being controlled.

Temperature control is a relatively young branch of automatic-control technology. As so often happens in a rapidly-developing art, the practical achievements of automatic temperature control have preceeded and far outstripped the literature available on the subject. In its present status, the principle objectives toward which efforts at analysis are being directed are:<sup>2</sup>

- (a) Development of a generally-accepted nomenclature.
- (b) Classification of the processes to be controlled and the methods of control.
- (c) Determination of time constants which, when inserted in the theoretical equations, will yield at least approximate solutions in the application of the theory of temperature control to practical problems, and which will define a "figure of merit" to describe the effectiveness of a given method of control in a given process.

A uniform terminology and an exact method for the application of temperature control would facilitate the interchange of pertinent, quantitative data between process equipment manufacturer, instrument manufacturer, control consultant and user.

### Classification of processes

The development of a mathematical description of typical processes and the methods of controlling their temperatures has, in most cases, proceeded from analogy with existing theory. German writers have sought to adapt the theory of speed governors in turbines and steam engines to the problems

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<sup>2</sup> The reader is referred to reports of the A.S.M.E. Committee on Industrial Instruments and Regulators, and to the numerous papers on temperature control appearing in recent volumes of the A.S.M.E. Transactions.

of temperature regulation.<sup>3</sup> Many American authors draw on hydraulic analogies for the classification and description of temperature control problems.<sup>4,5</sup>

The process whose temperature is to be controlled may be considered to be a series or parallel system of one or more thermal capacities separated from each other by resistances. The flow of energy from one capacity to another is accompanied by a decrease in energy level. In general, processes can be divided into

A. Single-capacity systems.

B. Multiple-capacity systems.

1. capacities and resistances in series.
2. capacities and resistances in parallel.
3. series-parallel combinations.

In analyzing regulation problems, it is customary to assume a linear differential equation (of second or higher order), the type which describes vibrating systems

$$\frac{c_2 d^2 \phi}{dt^2} + \frac{c_1 d\phi}{dt} + c_0 = 0$$

$\phi$  is the fractional deviation of the temperature from its standard value:  $(T - T_a)/T_a$ . For a given problem this equation must be reduced to a specific form and its coefficients evaluated. The effectiveness of the control can then be specified in terms of the time constants.

The characteristics of a process which favor precise control are:

1. Minimum delay in response of temperature at the point of measurement to a change in supply or demand of heat.

<sup>3</sup> M. Lang, *Z. tech. Physik.*, 14, 98 (1933).

See also the English translations of important foreign papers in the "Technical Memoranda on Automatic Control," published by the A.S.M.E. Committee on Industrial Instruments and Regulators (1938).

<sup>4</sup> A. F. Spitzglass, *A.S.M.E. Trans.*, 60, 665 (1938); 62, 51 (1940).

<sup>5</sup> C. E. Mason, *A.S.M.E. Trans.*, 60, 327 (1938).

C. E. Mason and G. A. Philbrick, *A.S.M.E. Trans.*, 62, 1 (1940).

2. Minimum transfer lag i.e., delay in response due to poor heat transfer (large resistance) in the heat exchanger.
3. Minimum temperature difference between the heater and the thermostat.
4. Minimum supply-side thermal capacity, relative to total thermal capacity.
5. Maximum demand-side thermal capacity, relative to total thermal capacity.

### Classification of control equipment

In automatic temperature control apparatus a temperature-sensitive element serves to increase or decrease the

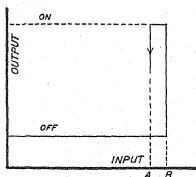


FIG. 94a.—Relay characteristics.

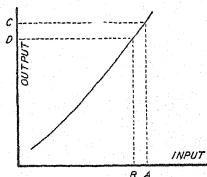


FIG. 94b.—Amplifier characteristics.

supply of heat to the body whose temperature is to be held constant, whenever its temperature passes a selected value. The sensitive element controls the heat supply either through a relay (discontinuous) or amplifier (continuous) device.

In a thermostat which uses a relay, the fundamental obstacle to attainment of perfect constancy of temperature is the discontinuous relation between the input and output of the relay, i.e., its “back lash.” In a thermostat which uses an amplifier, the relation between input and output is continuous. In this case it is the finite sensitivity of the amplifier which prevents attainment of perfect constancy of temperature. Only by making  $AB = 0$  in Fig. 94a or  $AB/CD = 0$  in Fig. 94b could a thermostat be made completely effective in resisting changes of the ambient temperature.

Automatic temperature control equipment may be grouped into four main classes:<sup>6</sup>

1. On-off, or two-position.
2. Floating.
3. Proportional.
  - Narrow-band.
  - Wide-band.
4. Proportional reset.

In fixed-position control the valve motion is rapid and the temperature range between adjacent control points is very small, practically zero in electric contact types. Fixed-position control has a discontinuous character.

In floating control (seldom used alone for temperature control) the valve motion is relatively slow, so that normally the on-and-off response of the instrument does not produce valve motions to the limits. Floating control may be adjusted to avoid the violent changes in the thermal-demand characteristic of on-and-off control. However, floating control cannot handle rapid or wide fluctuations in load as well as on-and-off control.

Proportional or throttling control refers to equipment in which the valve position is proportional to, or corresponds with, the temperature within a certain control band. The valve is closed at one side of the control band, or throttling range, and open at the other. For each intermediate valve position there is a corresponding temperature in the control band. As the load varies, corresponding valve openings and positions are required, and the controlled temperature wanders accordingly within the limits of the control band. This drift of the control point is often a serious limitation to the use of proportional control. However, proportional control normally operates by making minute and gradual adjustments. This characteristic is frequently desired, and in some

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<sup>6</sup> E. D. Haigler, *A.S.M.E. Trans.*, 60, 633 (1938).

cases may be required to avoid interaction of several controls on one system.

As the control band is widened the increments of control-valve travel for a given change in temperature are reduced, making the controlling corrections correspondingly less sudden and disturbing. But since the actual control point may be anywhere within the control band (depending on the load at the moment), wide-band control brings the possibility of great and perhaps excessive wandering of temperature with varying load conditions.

Proportional reset control provides for resetting automatically the relationship between temperature and valve position to compensate for the deviation of control point with load change. It is the only proportional control capable of high accuracy under varying loads.

### Practical fundamentals

In the performance of a control pyrometer it is time that counts—the time that elapses between the first small temperature change and the correcting motion of valve or other controlling device. Figure 95 shows the characteristic temperature-time curves which can be obtained by successive refinements in control methods.

Assuming the operator's consistent, undivided attention, manual control is capable of excellent results. Usually, however, fatigue on the part of the operator, and his attention to other duties, result in irregular temperature fluctuations.

Two-position (on-off) control overcomes any irregular fluctuations due to the human equation, and provides regular fluctuations within a uniform control band.

In proportional control, as previously stated, there is for each temperature within the control band a corresponding valve position. However, a sustained change in operating conditions will cause input and demand to balance above or below the control point. This effect is called a droop-characteristic. At any instant droop is the difference between the



actual temperature at which the process is being held and the temperature for which the control is set.

In proportional-reset control, a droop-corrector is added to the control equipment. Then when a sustained change in operating conditions occurs, the droop-corrector resets the throttling range (i.e. the portion of the instrument range which

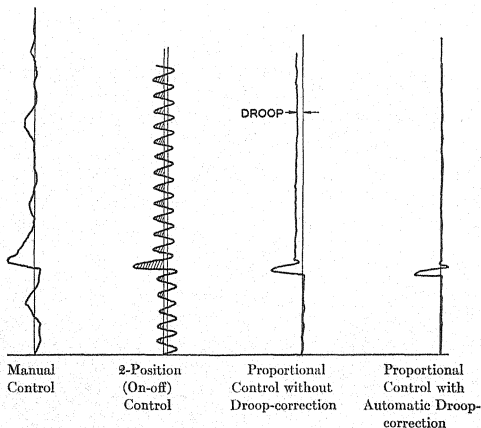
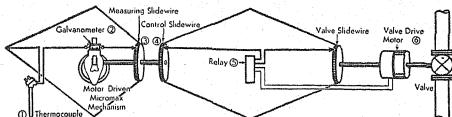
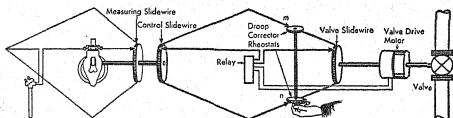


FIG. 95.—Characteristics of various control methods. (*Leeds & Northrup Co.*)

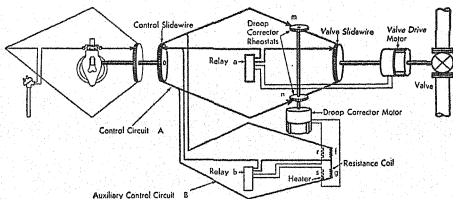
corresponds to full travel of the final control valve from maximum to minimum) to establish a new input which will hold temperature at the original control point. The valve is moved not only (1) as a function of temperature change, but (2) also as a function of both how long and how far temperature is off the control point. By regulating input in proportion to demand this type of control does more than hold temperature within close limits—it holds to a selected control point with a steadiness which, on many processes, is essential



The Basis of Proportional Control . . . In which there is a fixed relationship between the positions of control and valve slidewires, so that for any temperature there is a fixed valve position. In every proportional control there should be, however, a way to vary this fixed relationship—either manually or automatically as shown below.



The Manual Way—with manual droop-corrector . . . An operator watches the recorder chart, and, when necessary, turns rheostats “m” and “n” to establish a new relationship between control and valve slidewires.



The Automatic Way—with automatic droop-corrector . . . In place of the operator, there is a motor to turn the rheostat and an auxiliary control circuit which directs the motor. Auxiliary circuit action persists until temperature is at the control point.

FIG. 96.—Proportional electric control applies the balance principle both to measurement and to control. (Leeds & Northrup Co.)

to full efficiency, to fuel savings, and to increased process yield.

The way in which droop correction is applied is indicated in the explanatory notes accompanying Fig. 96.

The importance of the balance principle in temperature measurement has already been emphasized in the discussion

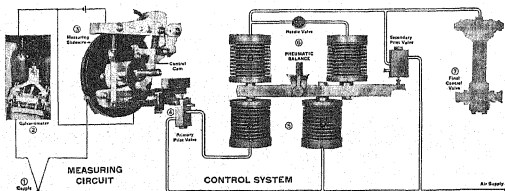


FIG. 97.—Elements of an automatic temperature control system using pneumatic control. (*Leeds & Northrup Co.*)

- ① Temperature changes cause unbalance in measuring circuit.
- ② Galvanometer deflects, engages balancing mechanism.
- ③ Mechanism turns both measuring slidewire and control cam as a unit—restoring balance in measuring circuit.
- ④ Cam, acting through levers, moves stem of primary pilot valve, causing it to produce a new pressure.
- ⑤ The new pressure acts at “A” on pneumatic balance arm—moving stem of secondary pilot valve; causing it to produce a new pressure over diaphragm of final control valve.
- ⑥ New pressure of secondary pilot valve acts also at “B,” restoring instantaneous equilibrium in the pneumatic balance. Immediately, however, pressures at “B” and “C” tend to equalize through needle valve. The new force thus produced at “C” causes further movement of arm and valve stem in same direction as before.
- ⑦ This action continues until pneumatic balance comes to equilibrium at a new position of its arm—when final control valve has assumed a new position such that input exactly balances demand and temperature is again at the control point.

of potentiometers. In automatic temperature control, the principle of balance is often used both in measuring circuit and in the control system (Figs. 96 and 97). The control system may be either pneumatic or electric. Electric control offers conveniences in many applications, while in refining and chemical industries, where there is an explosion hazard, the preference is often for the pneumatic type.

### Thermostats<sup>7</sup>

The temperature-sensitive element used in a thermostat is often a bimetallic strip (Fig. 98) or a liquid-filled bulb (Fig. 99) arranged to open or close a heater circuit when the temperature passes a selected value. The bimetallic regulator is set by adjusting the tension on the coil. A liquid-in-glass regulator is set by adjusting the level of the contact-making wire (Fig. 99) or the level of the liquid (Fig. 100). High sensitivity and small lag are obtained by using a large surface/volume ratio. The tube may be made of a number of small "fingers" connected at the top, or the surface increased by indentations as in Fig. 101. A rapidly-conducting metal foil, such as copper, is sometimes placed in the toluene bulb.

An a.c. bridge and amplifier for continuous control of furnaces and thermostats is illustrated in Fig. 103. The power output of the control circuit is doubled for a change of only 0.03% in the resistance of the regulating thermometer. The circuit regulates a heater of 500 w. power and maintains the temperature of an oil bath or furnace constant to within

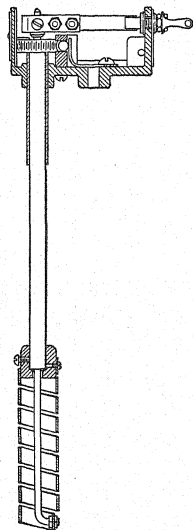
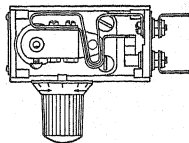


FIG. 98.—Bimetallic thermoregulator. (Central Scientific Co.)

<sup>7</sup> A. Lalande, *Les thermostats pour les températures moyennes*, Paris: Hermann et Cie., 1935. 54 pp.

R. Griffiths, *Thermostats and Temperature-regulating Instruments*, London: C. Griffin Co., 1934. 157 pp.

0.03°C. An elaboration of this type of thermoregulator employing a phase-shifting thyatron is illustrated in Fig. 103. The power output of the thyatron doubles for a decrease of about 0.003% in the resistance of the thermometer (cor-

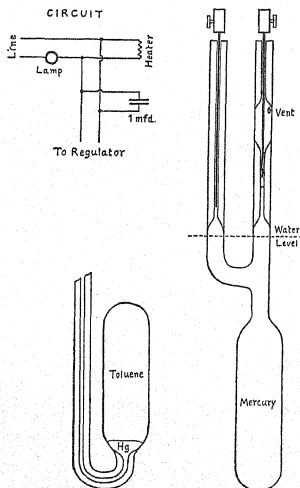


FIG. 99.—Types of liquid-filled thermoregulators and circuit. (J. S. Buck, *J. Chem. Education*, 13, 131 (1936).)

responding to a temperature change of 0.01°C.) and permits control of a water bath thermostat to  $\pm 0.003^\circ\text{C}$ . [This design has recently been improved by replacing  $R_3$  by a second thermometer element, which doubles the sensitivity. Also the plate supply for the FG57 has been isolated by a 1:1 transformer, omitting the connection marked X, and replacing  $R_3$  by an autotransformer.]

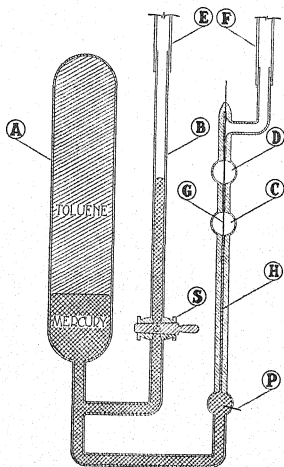


FIG. 100.—Adjustable thermoregulator. (H. B. Huddle, *J. Chem. Education*, 11, 569 (1934).)

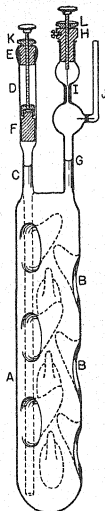


FIG. 101.—Adjustable sensitive thermoregulator. (J. Y. Yee and R. O. Davis, *Ind. Eng. Chem., Anal. Ed.*, 8, 477 (1936).)

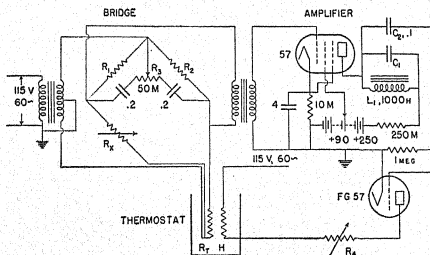


FIG. 102.—Resistance thermometer and a.c. bridge control circuit. (M. Benedict, *Rev. Sci. Instruments* 9, 252 (1938).)

## Control of furnaces and other heating devices

Bimetallic disks or rods provide an inexpensive means of controlling the temperature of electric irons, type-set-

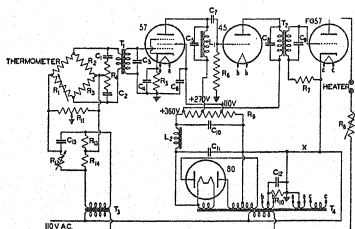
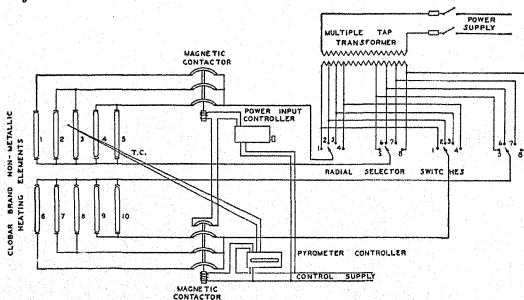


FIG. 103.—Circuit diagram of a thyatron thermoregulator. (J. M. Sturtevant, *Rev. Sci. Instruments*, 9, 276 (1938).)

ting melting pots or furnaces not requiring a wide range of adjustment.



WIRING DIAGRAM

FIG. 104.—Temperature control for an electric furnace. (The Carborundum Co., Globar Division.)

Thermocouples used with a recording-controlling potentiometer provide flexible control over a wide range of temperatures. Fig. 104 shows a control circuit for the laboratory

furnace illustrated in Fig. 147, Chap. XIV. The upper heating elements can be controlled independently of the lower ones. The current supplied to the upper heaters is regulated by a synchronous motor which determines the fraction of the time during which the circuit is closed. This is essentially the Gouy principle. The lower elements are put on or off the circuit by a relay actuated by a pyrometer controller in accordance with the temperature indicated by the thermocouple.

A resistance thermometer and bridge circuit is well adapted for controlling the temperature of an electric furnace. When the bridge becomes unbalanced, by a change in furnace temperature, its potential difference is made to alter the heating current, through the use of reflecting galvanometer and optical relay,<sup>8</sup> or an electron tube amplifier,<sup>9</sup> or a thyatron circuit.<sup>10, 11</sup>

Turner has made an interesting analysis<sup>12</sup> of self-oscillation in the control of an isothermal chamber and a comparison<sup>13</sup> of the theory with results obtained experimentally in an "academic oven." His conclusions, roughly stated, are:

1. Hunting, necessarily present if the heat supply is controlled in discrete quantities, will occur also when a continuous relation exists between temperature and heat supply, provided the control sensitivity exceeds a certain critical value. That is, stability of control is not necessarily improved merely by increasing the sensitivity of the temperature-sensitive device.<sup>14</sup>

2. Hunting does not depend on the thermal capacity of the chamber.

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<sup>8</sup> H. Moser, *Z. tech. Physik*, 13, 383 (1932).

<sup>9</sup> W. L. Walsh and N. A. Milas, *Ind. Eng. Chem., Anal. Ed.*, 7, 122 (1935).

<sup>10</sup> K. Henney, *Electron Tubes in Industry*, New York: McGraw-Hill, 1934. Chap. IV.

<sup>11</sup> R. M. Zabel and R. R. Hancox, *Rev. Sci. Instruments*, 5, 28 (1934).

<sup>12</sup> L. B. Turner, *Proc. Camb. Phil. Soc.*, 32, 663 (1936).

<sup>13</sup> L. B. Turner, *J. Inst. Elect. Eng. (Lond.)*, 81, 399 (1937).

<sup>14</sup> *The natural limit to the sensitivity of all measuring processes has been analyzed by R. B. Barnes and A. Silverman, Rev. Modern Phys.*, 6, 162 (1934).



3. The residual inconstancy of temperature does not depend on the thoroughness of insulation.

4. There exists a single figure of merit which measures the effectiveness of the equipment in resisting change due to ambient temperature and fluctuation of supply voltage.

5. The former factor is less important than the latter.

6. The effect of the difference in temperature between the chamber and the temperature-sensitive element must not be ignored.

7. The use of a single resistor for both the temperature-sensitive element and the heater, advocated by some workers, is wrong in principle.

One form of laboratory induction furnace is given a characteristic of self-regulation in the following manner. A hollow body of ferromagnetic material is traversed by a magnetic flux induced by a solenoid carrying alternating current. This is surrounded by a non-magnetic conducting envelope. Currents induced in the latter by the ferromagnetic material raise its temperature until the material reaches its Curie point (see Exp. 24), after which the temperature remains constant. The furnace can be made self-stabilizing for any temperature in the range  $15^{\circ}\text{C.}$  to  $1100^{\circ}\text{C.}$ <sup>15</sup>

Other methods of using temperature-sensitive magnetic alloys for temperature control have been described by Jackson and Russell.<sup>16</sup>

### Control of room temperature

Control of room temperature is one of the requirements of air conditioning in paper, textile and food industries and in dwellings. It is necessary to a higher degree of precision in rooms containing constant-frequency radio oscillators, animal calorimeters and spectroscopic apparatus.<sup>17</sup>

<sup>15</sup> R. Perin and V. Sorrel, *Compt. rend.*, **192**, 1026 (1931).

<sup>16</sup> L. R. Jackson and H. W. Russell, *Instruments*, **11**, (1938).

<sup>17</sup> W. E. Hoare, *Electrician (Lond.)*, **111**, 715 (1933).

Control of ordinary room temperatures is effected by the use of a bimetal or enclosed-liquid sensitive element, a relay, heater and adequate forced circulation of air.<sup>18</sup> Green and Loring have described a device which uses an ethyl ether vapor thermometer and relay to maintain the temperature (at a given location) in a laboratory constant to within  $0.05^{\circ}\text{C}$ . over long periods of time.<sup>19</sup>

### The Gouy principle<sup>20</sup>

An expansion thermometer of the type illustrated in Figs. 99 to 101 provides only discontinuous temperature control. The amount of lag depends on the sensitivity of the element, the degree to which the liquid sticks to the wire, etc.

Gouy designed a thermoregulator in which the contact-making wire (iron) was given a vertical oscillating motion of constant frequency (the period being 20 sec. and the amplitude 1.5 mm.). The time during the cycle during which the contact was closed varied from 0 to 20 sec. as the temperature difference changed from 0 to  $0.001^{\circ}\text{C}$ . This regulator, used with a relay and electric heater, permitted the temperature of a 100 l. water bath to be held constant within  $\pm 0.0002^{\circ}\text{C}$ . for several hours.

The Gouy principle is interesting because it represents the first device to bridge the gap between simple on-and-off control and continuous control. It is important because it is used, in modified forms, in many present day temperature controllers.

### References

- Adcock, F. "Apparatus for Raising or Lowering the Temperature of a Laboratory Furnace . . .," *J. Sci. Instruments*, 12, 285-288 (1935).  
ASME Committee on Industrial Instruments and Regulators, *Technical Memoranda on Automatic Control*, Chicago, 1938. [Translations of foreign articles.]

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<sup>18</sup> H. Barrell and J. C. Evans, *J. Sci. Instruments*, 12, 281 (1935).

<sup>19</sup> J. R. Green and R. A. Loring, *Rev. Sci. Instruments*, 11, 41 (1940).

<sup>20</sup> M. Gouy, *J. Physique*, 6, 479 (1897).

- Behar, M. F. *Fundamentals of Instrumentation*, Pittsburgh: Instruments Publishing Co., 1932.
- . *Temperature and Humidity Measurement and Control*, Pittsburgh. Instruments Publishing Co., 1932. pp. 111-420.
- Callender, A., Hartree, D. R. and Porter, A. "Time Lag in a Control System," *Phil. Trans. Roy. Soc.*, A235, 415-444 (1936).
- Henney, K. *Electron Tubes in Industry*, New York: McGraw-Hill, 1937. pp. 287-290; 398-407.
- Ivanoff, A. "Theoretical Foundations of the Automatic Regulation of Temperature," *J. Inst. Fuel*, 7, 117-138 (1934).
- Roebuck, J. R. "Mechanical Thermostats," *J. Optical Soc. Am. & Rev. Sci. Instruments*, 10, 679-690 (1925).
- Tilton, L. W. "Thermal Control in Minimum-deviation Refractometry . . .," *J. Research Nat. Bur. Standards*, 17, 389-400 (1936).
- Timoshenko, S. "Theory of Bi-metal Thermostats," *J. Optical Soc. Am. & Rev. Scientific Inst.*, 11, 233-255 (1925).

## CHAPTER X

# Calorimetry

### Introduction

Calorimetry is concerned with the measurement of energy in the form of heat. The attainment of high accuracy in such experiments is difficult, primarily because there exists no perfect heat insulator. The effects which are used to measure heat quantities are: change in temperature, change of state, and the transformation of electrical or mechanical energy into heat or vice versa.

Since it is impossible to deprive a body of all its heat, it is impossible to measure absolute, total heat content. Calculations are made from an arbitrary zero. The increase of heat content is found to be so nearly proportional to temperature increments that it is convenient to define the thermal capacity of a substance as the heat (calories) necessary to raise the temperature of 1 gm. by  $1^{\circ}\text{C}$ . The unit of heat, the calorie, is defined by making the thermal capacity of water unity. The specific heat of a substance is the ratio of its thermal capacity to the thermal capacity of water (a dimensionless ratio). However, specific heat is widely used as meaning the same as thermal capacity.

### Method of mixtures

If  $m$  grams of a substance at temperature  $t_1$  are added to  $M$  gm. of water initially at temperature  $t_0$  an exchange of heat results in the attainment of an equilibrium temperature  $t_2$ . The specific heat of the substance can be calculated from

$$s = \frac{M(t_2 - t_0)}{m(t_1 - t_2)} \quad (1)$$

This type of experiment is usually not susceptible of high accuracy. Principal sources of error are the heat losses and the thermometer readings.

### Steady flow electrical calorimeter

In the Callendar and Barnes apparatus, shown schematically in Fig. 105, an electric current is maintained in a resistance wire  $R$  placed along the axis of a narrow glass tube through which a constant stream of water flows. Inlet and outlet temperatures of the water are measured with platinum resistance thermometers. The flow of liquid and the electric

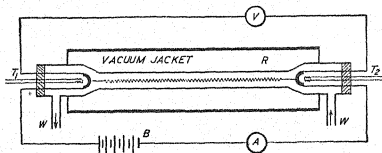


FIG. 105.—Constant-flow conductivity apparatus.

current  $I$  are adjusted to give a rise in temperature  $\Delta T$  of only a few degrees. From measurements of the power supplied,  $EI$ , and the mass of water  $M$  collected in a time  $t$ , the equation

$$EIt = JMs\Delta T + h \quad (2)$$

can be used to calculate the specific heat  $s$  of the liquid, or the mechanical equivalent of heat,  $J$ . The term  $h$  represents the heat lost by radiation, etc. If the experiment is repeated with a different flow and a different current, but with the same  $\Delta T$ ,  $h$  will be the same in the two cases and can be eliminated from the corresponding equations.

This type of apparatus has been used to show that the specific heat of water is not constant but varies with the temperature, passing through a minimum value at about  $38^\circ\text{C}$ .

### Low-temperature vacuum calorimeter

Measurements of specific heats at low temperatures are of particular theoretical interest. Figure 106 represents an adiabatic vacuum calorimeter of the type designed by Nernst and modified by Simon and Lang. The substance to be investigated is placed in a thin-walled copper vessel *A*. Inside of *A* are also a heating coil and a resistance thermometer. Surrounding *A* is a thermostat *B* equipped with a separate heating coil. Junctions of a differential thermocouple are placed in contact with *A* and *B*. By adjusting the heating currents to make the thermocouple indicate zero it is possible to keep  $T_A = T_B$ , and hence avoid heat loss.

The power supplied to the heating coil of *A* is  $EI$ . The temperature  $T$  is measured as a function of the time  $t$ . The value of  $dt/dT$  for any  $T$  can be evaluated from a graph of  $t$  vs.  $T$ . The heat capacity  $C_p$  for any temperature is given by

$$C_p = \left( \frac{\delta Q}{\delta T} \right)_p = \frac{EI}{J} \frac{dt}{dT} \quad (3)$$

### High-temperature vacuum calorimeter

Calorimetry in furnaces is undertaken to obtain information about metals at high temperatures. The experimental difficulties in achieving an accuracy of even 1 per cent are considerable, for (i) useful materials of construction become less available at high temperatures, (ii) it is harder to provide uniformity of temperature in the surroundings of the calorimeter, and (iii) the rate of heat loss from the calorimeter increases rapidly with temperature.

Figure 107 represents a high-temperature vacuum calorimeter of the copper block type. The five essential parts are:

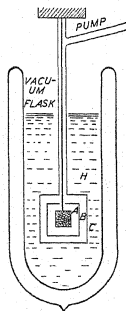


FIG. 106.—Low-temperature adiabatic vacuum calorimeter.

*A*, the copper block with a central hole into which the specimen is dropped; *B*, a guard system surrounding the block in order to control the heat loss from it; *C*, the furnace in which the specimen is heated to its initial temperature. The whole apparatus operates inside the evacuated vessel *D*, and the external furnace *E* maintains the block and its immediate surroundings at the desired operating temperature.

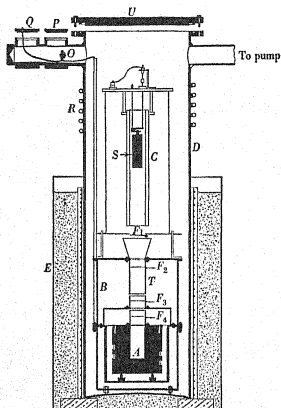


FIG. 107.—High-temperature vacuum calorimeter and furnace.

The specimen *S* is heated in the upper furnace *C*. It is then dropped into the copper block to which it gives up heat until the two are in thermal equilibrium. The product of the thermal capacity of the copper block and its rise in temperature on the introduction of the specimen, together with a correction for the heat lost by the block during the attainment of equilibrium, is equal to the difference between the heat content of the specimen at its initial and final temperatures.

### Constant-flow gas calorimeter

The heating value of a gaseous fuel can be measured by comparison with a standard source of heat in an apparatus of the type illustrated schematically in Fig. 108. When the thermometers 1 and 2 indicate the same temperature, the test gas is producing heat at the same rate as the standard source. The latter may be an electric heater or a burner consuming gas of known heating value.

Such a thermal balance calorimeter obviates the necessity for measuring a temperature rise in the working substance.

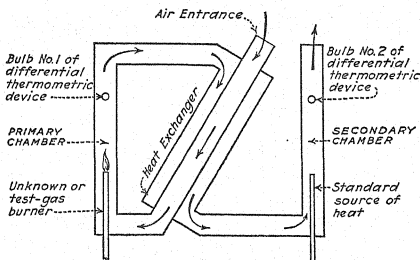


FIG. 108.—Diagrammatic representation of a thermal-balance calorimeter.

Being a null method, its accuracy is independent of the calibration of the temperature-measuring device. It compensates for heat losses, change in barometric pressure, room temperature or specific heat of the working substance. The method is readily adaptable to recording and controlling the heating value of gases, and hence has considerable industrial importance.

### Water pyrometer

The familiar calorimetric method of mixtures can be applied to the measurement of furnace temperatures, though its use has become less common with the development of



more convenient pyrometers. A water pyrometer comprises a test material, say a 100 g. block of nickel, a water calorimeter and a thermometer. The metal block is placed in the furnace whose temperature it is desired to measure. When the block has come to thermal equilibrium with its surroundings, it is quickly placed in the calorimeter, where it transfers heat to the water. From the known thermal capacity of the block and the measured weight of water and its temperature rise, the temperature of the furnace can be inferred.

### Potentiometer for calorimetric measurements

In calorimetry, it is often necessary to measure, practically simultaneously, two temperatures which are appreciably different and both changing rather rapidly, but at about the same rate. If these temperatures are to be indicated by thermocouples it is desirable to use a potentiometer of high precision and so designed that a single observer can follow minute changes in both temperatures with one instrument. High precision in a potentiometer is obtained by certain modifications in the simple circuits already described (Chap. IV), designed primarily to provide the following desirable characteristics: negligible effect of parasitic e.m.f.'s, low potentiometer resistance, constant potentiometer resistance across the galvanometer, freedom from switch contact resistance errors, and provision for maintaining a steady and precisely adjustable battery current. The convenience of being able to read two widely different e.m.f.'s with a minimum of readjustment is achieved by the use of a "double potentiometer."

To minimize the error from parasitic thermoelectromotive forces at moving contacts, and to make possible the use of compensating coils for keeping the galvanometer circuit resistance constant, it is desirable to use dial switches controlling a number of resistance coils, instead of using a slide-wire. With the slidewire changed to a number of resistance coils and with compensating coils added to keep the gal-

vanometer circuit resistance substantially constant, Fig. 29 of Chap. IV becomes Fig. 109.

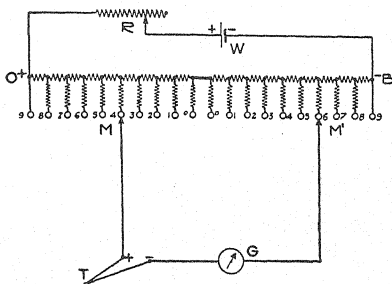


FIG. 109.—Potentiometer: compensating coils in galvanometer circuit. (*Leeds & Northrup Co.*)

A modification of Fig. 109 is shown in Fig. 110. In this case, the two switch contacts are in the battery circuit and the compensating coils are used to keep the battery circuit

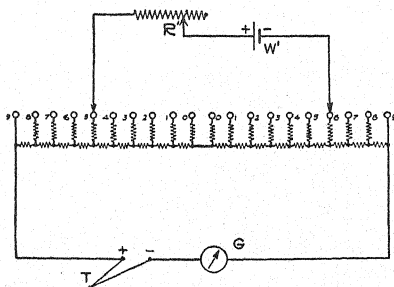


FIG. 110.—Potentiometer: compensating coils in battery circuit. (*Leeds & Northrup Co.*)

resistance constant for all positions of the switches. This is a considerable improvement over Fig. 109 for the low volt-

age dials of a potentiometer, because any parasitic e.m.f.'s produced at the sliding contacts are in series with the high battery voltage and, therefore, their effect is negligible.

With either arrangement shown, a difficulty arises in that only a finite number of steps is possible instead of the infinite number that can be obtained with a slidewire. Of course, by reading the unbalanced portion of the unknown e.m.f. from the galvanometer deflection, the exact value can be estimated, but deflection measurements are not sufficiently accurate for obtaining such a large part of the

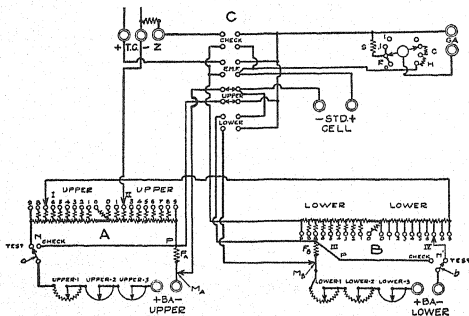


FIG. 111.—White single potentiometer. (Leeds & Northrup Co.)

total value. To obtain the small steps with the precision of adjustment that can be obtained with a slidewire, it is necessary to have more than two dial switches. In White potentiometers, the use of four dials is made possible by combining two potentiometers, one such as shown in Fig. 109 and the other such as shown in Fig. 110. The combined circuits are shown in Fig. 111 which also shows the connections in more detail and includes switches and current adjusting rheostats.

With this arrangement of circuits, the resistance in the galvanometer circuit is practically constant, so that the

portion of the emf which cannot be balanced out with the four dials can be read from the galvanometer deflection. The accuracy required in the deflection portion of the reading is very much less when four dials are used than when only two are used, so that high precision of reading and high accuracy are obtained.

It will be seen that the unknown voltage of the thermocouple is opposed to the voltage of the left or *upper* potentiometer *plus* the voltage of the right or *lower* potentiometer. The two lower voltage dials, which are the ones most frequently used when measuring temperature changes, are "neutral," or free from parasitic e.m.f.'s, because the contacts of the two lower dials are not in the galvanometer circuit, but are in the circuit in series with the high voltage of the auxiliary battery.

The circuits used in White potentiometers result in an instrument having a low resistance in the galvanometer circuit. This makes for high sensitivity in low voltage measurements, as the current which flows through the galvanometer for a particular voltage unbalance is inversely proportional to the total resistance in the galvanometer circuit. The low potentiometer resistance does not limit the use of the potentiometer to low-resistance circuits; if a high-resistance thermocouple is being measured a comparatively high-resistance galvanometer may be used.

The single potentiometer is intended primarily for the measurement of voltage of one thermocouple. If two thermocouples are to be measured, the White double potentiometer is convenient. If a single potentiometer were used to measure the voltage of two thermocouples differing appreciably in temperature, the dial setting would have to be changed each time the connections were changed. This might require more time than the operator could afford in making and recording the necessary observations. The double potentiometer is equipped with an extra set of dials, so that the two e.m.f.'s may be measured without resetting dials. In other

words, the dial settings may be made independently for the two thermocouples, connections being made to the same galvanometer alternately with a master switch.

The circuits for a double potentiometer are shown in Fig. 112. It will be seen that connections to the resistances of each potentiometer dial may be made by two independently adjustable contacts. Contacts  $P_1, P_2, P_3$  and  $P_4$  constitute one group and  $Q_1, Q_2, Q_3$ , and  $Q_4$  the other group. One group

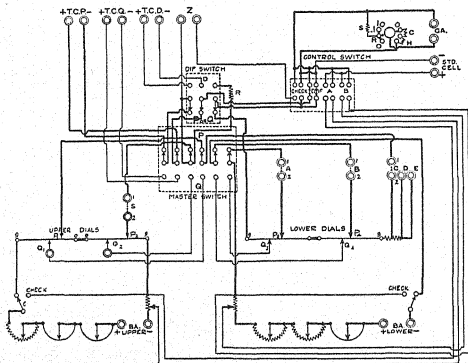


FIG. 112.—White double potentiometer. (Leeds & Northrup Co.)

of contacts may be set to the approximate voltage of one thermocouple, while the other group is set to the approximate voltage of another thermocouple. By means of a master switch, the galvanometer may be connected with one group of dials or the other and in each case the voltage increment above the respective dial settings is apparent, immediately, from the galvanometer deflection.

A convenient feature of the double potentiometer is the provision for differential measurements. A difference couple may be connected through a selector switch to the control

switch and to the galvanometer. A compensating resistance keeps the sensitivity of the galvanometer the same as it was when used as a deflection instrument in the regular measurements. The combination of couple and galvanometer constitute a direct deflection arrangement, which enables the operator to determine small temperature differences more quickly and accurately than were he to use independent couples and subtract.

Finally, the White potentiometer is arranged for making external connections for self-checking. The checking is done by opposing the fall in potential in any coil of the upper potentiometer to that of a section in the lower potentiometer.

### Resistance bridge for calorimetry

When the temperature measurements needed in calorimetry are made with a resistance thermometer, a bridge designed for high precision is required. Designed primarily for calorimetry, the Mueller bridge is a modification of the conventional Wheatstone network which provides higher accuracy over a comparatively narrow range. By measuring temperature changes in calorimetry with an accuracy comparable to, or higher than, that of the weight measurements, Mueller bridges increase the accuracy with which heats of combustion of coals, gases, oils and other fuels are determined. A Mueller bridge in combination with a suitable resistance thermometer is capable of greater accuracy between  $-190$  and  $500^{\circ}\text{C}$ . than any other means available.

Slight changes in value occur in the resistors of a bridge when they are subject to temperature variations. Obviously for measurements of highest precision it would be desirable to apply temperature corrections to the resistance calibrations, or, better, place them in a constant temperature chamber and thus eliminate the need for tedious corrections for ambient temperature. For routine testing, an unthermostated Mueller bridge is capable without ambient temperature corrections of measuring resistance change of from 0 to 0.6 ohm to a

limit of error of  $\pm 0.0001$  ohm. Equipped with a constant temperature chamber for the most important measuring resistors, the type G-2 Mueller bridge provides resistance measurements within a limit of error of a few hundred-

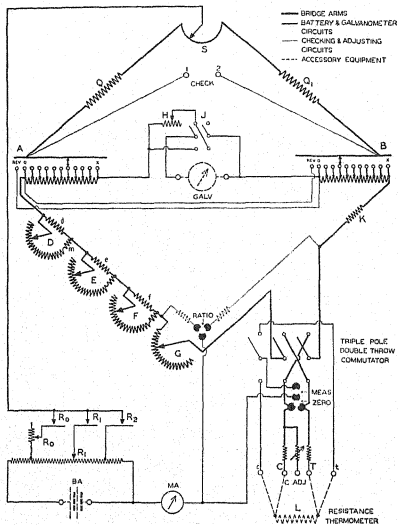


FIG. 113.—Circuit of the type G-2 Mueller bridge. (Leeds & Northrup Co.)

thousandths of an ohm, or a few parts per million, whichever is larger.

The Mueller circuit (Fig. 113) is essentially that of a conventional Wheatstone bridge. Decades *A*, *B*, *D*, *E*, *F* and *G* comprise the measuring resistors; *Q* and *Q*<sub>1</sub> are ratio arms; *L*, the thermometer coil, is the resistance to be measured.

The construction of the measuring arm is distinctive in that the 1 and 0.1 ohm decades (*A* and *B*) are permanently

connected in series with the galvanometer. These decades, at the ends of the ratio arms, have the effect of transferring resistance between the lower arms of the bridge and the galvanometer circuit. When in the galvanometer circuit, resistance has no effect upon balance. Increasing the setting of decade *A* inserts resistance directly into the measuring arm. Increasing the setting of decade *B* takes resistance out of the thermometer arm which has the same effect as putting resistance into the measuring arm. Terminals

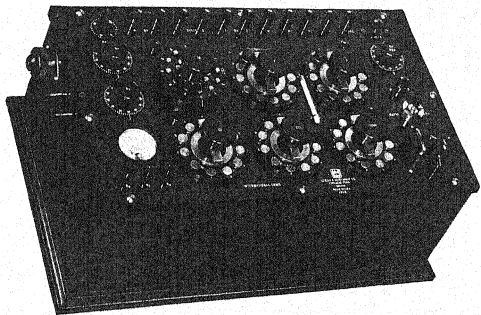


FIG. 114.—Mueller-type temperature bridge. (*Leeds & Northrup Co.*)

“1 Check 2” are provided for checking the equality of resistance of leads between resistors and studs in decades *A* and *B*.

The resistances of the contacts of decades *A* and *B* are of negligible consequence, being in series with comparatively high resistance ratio arms  $Q$  and  $Q_1$ . Contact resistances in the three lowest decades of 0.01, 0.001 and 0.0001 ohm (*D*, *E* and *F*) have a negligible effect on results as these decades are so constructed that a permanently connected resistor of low value is shunted by a comparatively high resistance in series with the contact. A low-resistance mercury-cup copper-bar switch controls the ten-ohm decade



*G.* Leads to its resistors are equal in resistance, as are the leads from all resistors of decades *A* and *B* to their respective switch studs. Leads to the ratio resistors and leads to the ratio reversing points of decades *A* and *B* are also equal.

With all dials on zero, there exists a residual resistance in the measuring arm due to the construction of decades *D*, *E* and *F*. Balanced against this residual is the resistance of decade *B* plus the resistance of the coil *K*. The sum of these two resistances is slightly greater than the residual of the measuring arm, so that when the thermometer arm is short-circuited by inserting a plug in the hole marked "zero," a small portion of the measuring arm is necessary to balance the bridge. This "zero reading" must be subtracted from subsequent measurements to obtain the true resistance of the thermometer.

The ratio arms  $Q$  and  $Q_1$  are joined by a slidewire *S* and are interchangeable. By moving the battery contact along the slidewire, the ratio can be adjusted to an equality which is only limited by the sensitivity of the galvanometer and the adjustability of the slidewire.

In addition to the plug position for obtaining the zero reading, another position is provided to make connections for quick and accurate adjustment of the ratio to equality.

To measure the resistance between the branch points of a four terminal thermometer, that is, the resistance between the potential terminals of a thermometer provided with current and potential terminals, two readings are required. With the commutator in the normal position, the battery supply lead is the one marked *c*, and the bridge is balanced with the lead *C* in the measuring arm, and  $L + T$  in the measured arm. With the commutator in the reversed position, the lead marked *t* becomes the battery supply lead, and the bridge is balanced with the lead *T* in the measuring arm, and  $L + C$  in the measured arm. The average of the two balances, except for the correction for bridge zero, represents the resistance of *L*.

Important internal leads to the commutator are equal in resistance. The terminal *CADJ.* is provided to be used in place of terminal *C* when the bridge leads to the thermometer element are not practically equal in resistance. A variable resistor in series with *CADJ.* is then adjusted to equalize the resistance so that the two bridge readings, with the commutator normal and reversed, are nearly equal.

Current is provided by from one to five dry-cells in series, with resistors connected across them. Three keys  $R_2$ ,  $R_1$  and  $R_0$  tap off different potentials providing low, medium and high sensitivity respectively. Currents provided by keys  $R_1$  and  $R_0$  are variable. When measuring, the current in the thermometer can be adjusted to the same value as that at which it was calibrated. Thermometer current is indicated on a milliammeter.

The switch and variable resistor in the galvanometer circuit provide adjustable series or parallel resistance for damping.

### Summary

Determination of the heating value of fuels and the specific heats of solids, liquids and gases is based on calorimetry. Calorimetry is the measurement of heat quantities in terms of temperature changes, changes of state or the transformation of electrical or mechanical energy into heat. Principal sources of error are the thermometer readings and heat losses. The latter are minimized by corrections from blank experiments, or in the method of mixtures by insuring adiabatic conditions. The temperature measuring instruments customarily used in calorimetry are, in order of accuracy: resistance thermometers, thermocouples and mercury-in-glass thermometers.

### References

- White, W. P. *The Modern Calorimeter*, New York: Chemical Catalog Co., 1928.  
Hyde, C. G. and Mills, F. E. *Gas Calorimetry*, London: E. Benn, 1932.

## Thermal Analysis

### Statement of the phase rule

The progress of physical science is marked by a multitude of isolated experiments and the rarer synthesis of their results into laws or theories which unify whole fields of the science. One of the monuments of nineteenth century scientific activity was the treatise by Josiah Willard Gibbs "On the Equilibrium or Heterogeneous Substances." In it he formulated the phase rule which deals with systems in equilibrium. It is usually expressed by the formula,

$$F = C - P + 2 \quad (1)$$

showing the relations existing between the degree of freedom  $F$  of the system, the number of components  $C$  and the number of phases  $P$ .

To understand the phase rule and its application it is necessary and sufficient to have an accurate understanding of the meaning of the terms employed in its statement. A system is that part of the physical world being considered. It may be separated from its surroundings by definite boundaries, or the boundaries may be imaginary.

A system is said to be in equilibrium when the net rate of any possible chemical changes within it is zero and there is an absence of molecular transformations (changes of state or allotropic changes). A system in equilibrium cannot alter with time without gain or loss of energy. In thermodynamic terms, its free energy is a minimum or its entropy a maximum. The phase rule is often applied also to systems

whose free energy is not a minimum, but whose properties do not change appreciably during the time of observation.

The phases of a system refer to its homogeneous parts separated from one another by definite physical boundaries. Water, ice and vapor, for example, are phases possible in the water system. It is apparent that phases are necessarily elements, gaseous mixtures, chemical compounds or solutions.

The components of a system are the chemical substances required to make the phases in any quantity in which they may be present. The choice of the independent components of a system is somewhat arbitrary. The number of independent components of a system is the smallest number of independently variable constituents from which the phases can be made in any relative quantities. That is, the number of independent components equals the total number of components minus the number of equations existing between the components. The number of components of a system is understood to mean the number of independent components.

By the degree of freedom, or variance, of a system is meant the number of variables which may be arbitrarily changed without disturbing the equilibrium of the system. The variables commonly considered in defining the state of a system are composition, temperature and pressure.

As a simple example, apply the phase rule to the system of ice and water in equilibrium. It is a one component system. From Eq. 1, the degree of freedom is  $1 - 2 + 2 = 1$ . If it is decided to hold the system at a given temperature the pressure is determined, and vice versa. The phase rule applied to a system of ice, water and vapor gives a variance of zero. The presence of three phases in a system of one component fixes both the temperature and the pressure. Only at the triple point and under the vapor pressure of ice can all three phases exist in equilibrium.

Consider further the equilibrium system represented by



There are in all three components, connected by one equation. Hence the number of independent components is two. These may be chosen as any of the following pairs:  $\text{CaO}$  and  $\text{CO}_2$ ;  $\text{CaO}$  and  $\text{Ca}_2\text{O}_3$ ; or  $\text{CO}_2$  and  $\text{Ca}_2\text{O}_3$ . The degree of freedom is:  $2 - 3 + 2 = 1$ . Hence for a given temperature, the  $\text{CO}_2$  has a definite pressure, independent of the quantities of the substances. If the lime burning is carried out in air (assumed pure  $\text{N}_2$ ), then the total number of components is four and the degrees of freedom two. Then for a definite temperature, the pressure of  $\text{CO}_2$  can have any value. Whether the partial pressure of  $\text{CO}_2$  is independent of the total pressure is a question for experiment, it is not determined by the phase rule.

### Deduction of the phase rule

The deduction of the phase rule consists in finding the total number of variables which may determine the properties of a system and subtracting from this the number of independent equations connecting those variables. Thus the number of variables whose values must be specified to determine completely the properties of the system is found. A distinction is made between extensive properties, such as volume and energy, which depend on mass, and intensive properties, such as temperature and pressure, which are independent of mass.

The following assumptions are made:

- (i) For two equilibrium systems to be identical there must be similarity in the quantities, by weight, of the components as well as total energy and total volume.
- (ii) Only those cases are considered in which this condition regarding the components is satisfied. Included are all cases which are in complete equilibrium and which are not acted on by outside forces except those due to the pressure of surrounding walls.
- (iii) The quantities by weight of the phases are independent of one another.
- (iv) There is no relation between quantities of the phases and the intensive properties.

The weights of quantities of the independent components ( $C$  in number) will be designated by  $G_i$ . The phases ( $P$  in number) will be designated by  $G^{(j)}$ . The total energy and total volume of the system will be represented by  $U$  and  $V$  respectively. The quantities  $G_i$ ,  $U$  and  $V$  which characterize the system completely (i.e., all its properties) can be transformed in the following manner:

$$G_i = \sum_j G^{(j)} n_i^{(j)} \quad i = 1, 2, 3, \dots C; \quad j = 1, 2, 3, \dots P$$

$$U = \sum_j G^{(j)} e^{(j)}$$

$$V = \sum_j G^{(j)} v^{(j)}$$

The  $n_i^{(j)}$ ,  $e^{(j)}$  and  $v^{(j)}$  are intensive quantities, whose exact meaning is unimportant in the derivation above. Since the system is defined completely by the  $C + 2$  variables to the left in the equations above, of the quantities on the right only  $C + 2$  are independent. By assumption (iii) the  $G^{(j)}$  always can be taken as independent variables. By virtue of (iv) there is dependence among the intensive quantities on the right such that merely  $C + 2 - P$  of them are independent. From (ii) and (iv) it then follows that any arbitrary intensive property is defined by these  $C + 2 - P$  intensive variables.

The phase rule is essentially a qualitative relation. It must be extended by experimental data to give quantitative information about a system to be of practical utility. Such information is conveniently represented graphically in what are called equilibrium diagrams, phase diagrams or phase rule diagrams.

### Cooling curves

Temperature-time curves, usually taken during cooling, provide an important method for studying phase changes in metals and alloys and for measuring specific and latent heats. Any change in state or constitution is accompanied by an energy change which is revealed by heat evolution during cooling or heat absorption during heating. When a body cools without such change occurring its cooling curve has the logarithmic form of *A*, Fig. 115. If the specimen is

molten metal, regular cooling is arrested by the heat evolved when the metal solidifies. If no undercooling occurs, the cooling curve has the form of *B*. However, the beginning of solidification is always accompanied by some undercooling. Nuclei do not become sufficiently stable to serve as starting points for crystallization until the melt is cooled to a temperature lower than the highest temperature at which solidification can occur. Actual cooling curves for pure metals resemble curve *C*.

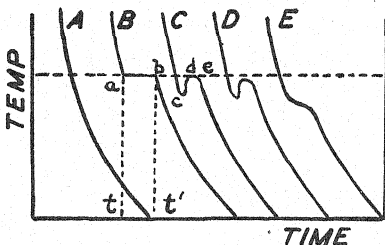


FIG. 115.—Cooling curves.

The exact form of curve obtained after freezing begins depends on the relation between the rate of removal of heat from the cooling metal and the rate of evolution of heat of crystallization. The time  $t_1 - t_2$  required to abstract a given amount of heat depends on the rate of cooling.

The rate of evolution of heat (rate of solidification) does not always keep pace with the rate of abstraction of heat. Solidification begins below  $T_1$ , as at point *c* in curve *C*. If there is no limit on the rate of solidification, other than that  $T$  cannot exceed  $T_1$ , then the heat evolved will raise  $T$  to  $T_1$ , and keep it there during the solidifying process (giving *cde*, curve *C*). If, however, there exists some limitation on the rate of solidification, conditions are different. It actually appears that for each temperature below the freezing point a definite maximum rate of solidification exists. This is

comparatively small at the freezing point, increases to a maximum, then decreases as the temperature is lowered. Hence for rapid cooling the temperature after undercooling may not reach  $T_1$ , giving a curve of the form *D*.

In the ideal case, the temperature of the metal will remain constant during melting and freezing, with the result that the portions of the curves *AB* and *A'B'* (Fig. 116) respectively, will be flat and parallel to the time axis. The ideal curve is further characterized by a discontinuous change of slope, rather than by a gradual change, as shown.

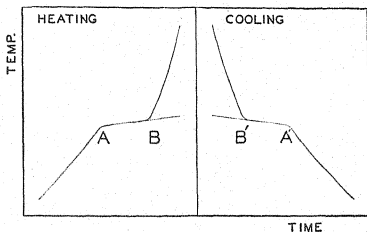


FIG. 116.—Heating and cooling curves for a pure metal.

In the actual case, however, only a part of the cooling curve will be flat, and this part of the heating curve will usually have greater obliquity than the freezing curve. Because of this, freezing point determinations are considered more reliable. For practical purposes, they may be considered equal to melting points.

The reason for obliquity and its existence to a greater degree in the heating curves is partly due to conditions relating to equipment and technique employed in obtaining data. When a crucible of metal is uniformly heated in a furnace, a temperature gradient exists between the walls of the furnace and the crucible. The metal in immediate contact with the crucible is the first to melt, and during the process of melting, the heat necessary for fusion is supplied



by the walls of the crucible and the remaining solid metal. The melted, outside layer of metal then tends to remain at fairly constant temperature. The temperature-measuring instrument, located in the center of the charge, measures the temperature of the solid metal and, since heat is being abstracted from this portion of the charge, the rate at which the inside temperature increases is greatly diminished with the result of a rounding off of the curve.

As the metal progressively melts inward, the temperature of the center metal rises slowly. When the metal surrounding the thermocouple melts, the temperature remains fairly constant for a short interval of time and indicates the true melting point, as represented by point *B* in Fig. 116. While the center of the charge is melting, the temperature of the outside layer of molten metal rises rapidly, owing to the heat supplied from the furnace walls. A large temperature gradient is thus established between the outside and the center of the charge. This temperature gradient promotes rapid melting of the metal and, if the remaining solid metal is unevenly distributed about the thermocouple, causes the temperature readings to increase, resulting in another rounding off of the curve. The degree of obliquity at the beginning and at the end of melting depends to a great extent upon the sensitivity of the temperature-measuring instrument and, of course, the coordinate scales used in plotting. In addition, the obliquity is governed by such factors as the size and wall thickness of the crucible, the amount of metal constituting the charge, and the rate at which the charge is heated. It may be diminished by slow heating and a small amount of charge.

Upon cooling of the molten metal, a temperature gradient exists between the crucible and the walls of the furnace. The metal in immediate contact with the walls of the crucible is the first to solidify, forming an isothermal layer, which decreases the temperature difference between the center and the outside of the charge. This, in effect, decreases the

rate at which the temperature falls at the center of the charge, thereby causing a rounding off of the first part of the cooling curve. During the freezing of the center of the charge, the solid outside layer of metal drops in temperature, thus increasing the temperature gradient between the center and outside portions of the charge. The freezing of the last traces of liquid metal is thereby accelerated, with the result that the last part of the curve is rounded off.

It is evident, therefore, that the first part of the approximately flat portion of the cooling curve and the latter part of the flat portion of the heating curve indicate the true freezing and melting points, respectively. Whenever considerable obliquity is present, the true temperature of freezing may be obtained by extrapolating the straight portion of the cooling curve and noting at what temperature the constructed straight line deviates from the original curve. In like manner, the true melting temperature may be obtained from the heating curve. This method of extrapolation is shown at points *B* and *B'* respectively, in Fig. 116. In general, cooling curves are more sharply defined than heating curves of the same metal, and are, therefore, more frequently used to obtain transformation data.

There are four principal ways of recording cooling curve data in thermal analysis.

*Direct cooling curves*, while easy to obtain and to interpret, have several disadvantages. They become progressively less steep, and hence less sensitive to heat changes, as the temperature of the specimen falls. It is difficult to detect transformations which involve small heat changes. In practice the time required for the stabilization of conditions following a major heat effect in the specimen makes it difficult to detect any small heat effects which may occur only a few degrees lower.

*Inverse rate curves* are obtained by plotting as ordinates the temperature, and as abscissas the time required for the temperature to fall through successive equal intervals (of the

order of  $2^{\circ}$ – $5^{\circ}$ ). Merica has suggested a method of obtaining the time intervals with two stop watches. One is stopped and the other started at the end of each time interval. During each time interval, it is thus possible to record the length of the preceeding interval.

*Differential curves* are obtained with the metal under study, cooling, beside another sample known to undergo no phase changes in the temperature range investigated. The temperature of the metal under test is plotted against the difference in temperature between it and the inert sample. If no changes involving latent heat effects occur, the curve

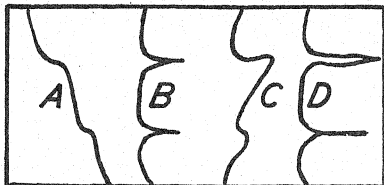


FIG. 117.—Cooling curves: A, direct; B, inverse rate; C, differential; D, derived differential.

is a vertical line. But if such changes occur, cooling is delayed and the curve departs from the vertical.

*Derived differential curves* have temperature plotted against the slope at each point of the curve showing the difference in temperature for the two samples.

These four methods of recording cooling data are illustrated in Fig. 117, which shows their relative sensitivity in locating transition points.

### Equilibrium diagrams

The state of a two-component system may be represented by a point on a three-dimensional diagram in which composition, temperature and pressure are plotted. For metallic systems the effect of pressure is not important, and a two-

dimensional temperature-composition diagram suffices to describe the conditions of equilibrium in the system. The vapor phase is omitted since the vapor pressure of metals is usually negligibly small.

Figure 118 is a generalized equilibrium diagram for a two-component system in which no compounds are formed. Under equilibrium conditions, an alloy begins to solidify when cooled to approach a point on line  $T_1ET_2$ . If the composition of the alloy lies to the left of  $E$ , solidification begins when it is cooled to line  $T_1E$  and solid  $A$  is deposited. If the

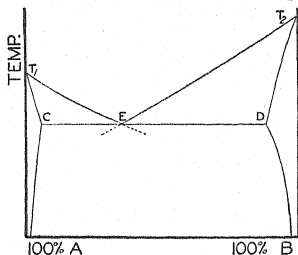


Fig. 118.—General eutectic diagram.

composition lies to the right of  $E$ , solidification begins when the alloy is cooled to line  $ET_2$  with the deposit of solid  $B$ . Point  $E$ , representing the eutectic temperature and composition, owes its significance to the fact that it lies on both lines. If liquid of composition  $E$  is cooled below the temperature  $E$  crystals of  $A$  and  $B$  may form simultaneously.

The areas at the side of Fig. 118 represent the existence of solid solutions in the A-rich and B-rich alloys, respectively. A solid solution is a homogeneous crystalline phase containing both components, but in indefinite proportions (not in atomic or molecular ratios as in a compound). Some substances form solid solutions in all proportions, just as some liquids mix in all proportions. Other substances have only limited solubility in each other.

It is important to distinguish between a solid solution and an eutectic mixture. A solid solution is a single crystal containing two kinds of atoms or molecules. It is one phase. An eutectic mixture is a mixture of pure crystals of each component. These often solidify in alternate thin layers or plates, and are separable. Hence there is no such thing as an "eutectic phase." The eutectic mixture is that intimate mixture of two solid phases which solidify from the liquid of lowest solidifying temperature.

Figure 119 is a temperature-composition diagram for the Cd-Bi system. At the side, Fig. 120, are examples of cooling

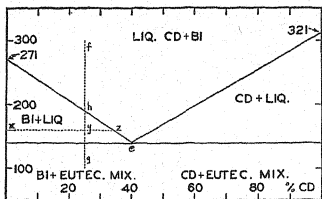


FIG. 119.—Cd-Bi equilibrium diagram.

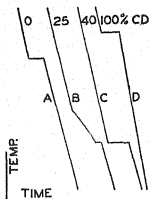


FIG. 120.—Cd-Bi cooling curves.

curves for different compositions of the Cd-Bi alloy. Consider an alloy of 25% Cd which has been heated well above its melting point and allowed to cool. The cooling may be represented by the temperature-time curve *B* of Fig. 120, or by the dotted line *fg* in Fig. 119. At 180°, Bi will begin to solidify from the melt, changing the rate of cooling. The remaining liquid will become richer in Cd, the point representing its composition following along curve *hze*. When the eutectic composition is reached and the temperature still further lowered, a liquid phase is no longer possible and the remaining liquid freezes at a definite temperature (140°) and composition (40% Cd). This is an exothermic change resulting in a pause in the cooling curve *B*, Fig. 120.

### Experimental method

The furnace for obtaining thermal data should be capable of heating the charge uniformly to the highest temperature required and should be so insulated that the specimen may be allowed to cool at a moderate, uniform rate. A satisfactory rate of cooling is about  $2^{\circ}\text{C}$ . per minute from  $10^{\circ}\text{C}$ . above the melting point, and the flat portion of the curve should extend a distance equivalent to about 10 minutes on the time axis. Furnaces that are neither properly designed nor sufficiently insulated will result in a non-uniform rate of cooling. This will affect the shape of the curve and may introduce irregularities that will mask important transformation points.

In the preparation of the charge, if the metal is to be heated for the first time, it should be broken into small pieces, placed in a crucible of the proper size and composition, and heated approximately  $10^{\circ}\text{C}$ . beyond the melting point. The surface of the molten metal, except when it is nickel, should be covered with a layer of graphite, to prevent oxidation of the metal. Small amounts of oxide in a pure metal, such as in copper, may appreciably alter the shape of the cooling curve and indicate the occurrence of transformations at temperatures lower than normal.

The selection of a crucible that is to hold the charge is of considerable importance. For most metals, crucibles composed of Acheson graphite are found satisfactory. At high temperatures the gases formed from its oxidation provide a reducing atmosphere which, in addition to the powdered graphite, protects the surface of the molten metal. Metals—such as iron and nickel—that react with graphite at high temperatures, should be melted in crucibles composed of magnesia or alumina, or mixtures of the two.

Accurate results are obtained only when the metal bath and the thermocouple wires are protected from contamination. The metal bath may be protected as described above, and the thermocouple by means of a suitable protecting tube.

For low-temperature work, up to approximately 500°C., pyrex-tubing, sealed at one end, serves very well. The use of porcelain or quartz protecting tubes is recommended for higher temperatures and with all metals except aluminum, which readily attacks silica at high temperatures. Above 1100°C. protection tubes having a composition approximating that of sillimanite are available.

Figure 121 illustrates a furnace for thermal analysis<sup>1</sup> whose temperature may be maintained a constant amount above or below the specimen temperature. This apparatus not only provides conventional cooling curves, but also permits quantitative measurements of specific heats and latent heats.<sup>1</sup> Another advantage is that it makes possible the detection of any small heat effect at a temperature only a few degrees below that at which a major effect has occurred. (With the conventional differential-thermocouple analysis method, sufficient stabilization after a large heat effect for the detection of a small one may not occur until the furnace has reached a temperature as much as 30 to 50°C. from that at which the large effect occurred.)

The specimen is placed in an insulating refractory container across which a constant temperature gradient is automatically maintained by the use of a differential thermocouple and a controller. Two ways of connecting the differential couple are shown in Fig. 121. Heat flow to the sample depends only on the constants of the container, which may be determined by the use of a sample of known specific heat. The time taken to cool or heat through a given temperature interval (after correction from a blank experiment) is directly proportional to the heat capacity of the sample, and the duration of the arrest is directly proportional to the latent heat. The method of control eliminates accelerated cooling following prolonged arrests and provides a simple way of obtaining a constant cooling rate at all temperatures.

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<sup>1</sup> C. S. Smith, *Am. Inst. Mining Met. Engrs.*, Tech. Pub. 1100 (1939).

These advantages may be increased by substituting for the refractory container of Fig. 121, two concentric nichrome cylinders, inside of which is placed a very thin walled cruci-

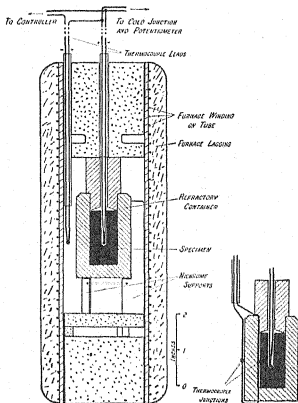


FIG. 121.—Furnace for thermal analysis.

ble, say, of graphite. Alumel wires welded to the nichrome cylinders form multi-junction thermocouples for controlling the temperature difference between the cylinders.<sup>2</sup>

Methods of thermal analysis have been applied to specimens as small as 0.1 gm. The samples are sealed in silica tubes, and difference curves obtained with a thermopile used in a high-temperature, thermostated furnace.<sup>3</sup>

### Dilatometry

The methods of thermal analysis so far described are primarily for use in determining transformations of state

<sup>2</sup> G. Edmunds, Discussion of preceding paper.

<sup>3</sup> W. E. L. Brown, *J. Sci. Instruments*, **16**, 195 (1939).



that are accompanied by marked thermal changes. Their sensitiveness depends to a great extent upon the rate of heating and cooling, and, because of this, they fail in detecting transformations in solid solubilities with constituents having slow reaction rates. Furthermore, the quantitative comparison of reaction rates is delicate and when the speed varies between wide limits, it is practically impossible to study the phenomenon by ordinary thermal methods.

Fortunately other methods are available. Transformations which occur in many metals and alloys, most notably steel, can be detected by quenching a series of specimens from temperatures progressively nearer the transformation temperature and noting the progress of the change, as made apparent in the microstructure. This method is of special value in determining solid-solubility lines or studying conditions where it is difficult to obtain true equilibrium. One serious difficulty, however, is encountered in this method: certain structural changes may take place during the time required to remove the specimen from the high temperature zone of the furnace to the quenching medium.

The temperature at which transformations occur in steel which are accompanied by changes in the magnetic susceptibility of the alloy may be detected by a method which uses the dip of a magnetic needle to detect these changes.<sup>4</sup>

Another method frequently used in determining solid solubility changes is electrical resistivity measurements of the metal under investigation. This method is useful over wide ranges of temperature and is particularly convenient and accurate for determining solidus lines. The results, however, are affected by such secondary factors as the thermal history of the metal and the presence of small amounts of impurities.

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<sup>4</sup> A. Sauveur, *The Metallography and Heat Treatment of Iron and Steel*, Cambridge: Harvard Univ. Press, 1935. p. 124.

In most metals transformation occurring in the solid state are accompanied by an expansion or contraction of the metal. By the use of sensitive measuring devices, this linear dilatation of the metal at the transformation points may be detected and subsequently correlated with the transformation temperatures. The phenomenon of volumetric changes at transformation points is illustrated in the heating and cooling of pure iron.

Iron crystallizes in the cubic system, being body-centered at room temperature, but changing to face-centered at about  $910^{\circ}\text{C}$ . In the rearrangement of the atoms to form the face-centered cubic lattice, the atoms become more closely packed, with the result that a marked contraction of the metal takes place. Upon its cooling, the reverse holds true. The atoms are then rearranged in the lattice to form a body-centered structure, causing the metal to expand. By the addition of carbon or alloying elements to the iron, the magnitude of the dilatometric effects is altered. As the carbon content is increased to the eutectic composition (0.83 per cent carbon), the volumetric changes become more pronounced, but they diminish in effect as the carbon content is further increased.

The study of the dilatometric characteristics of a metal or an alloy is best carried out by the use of a dilatometer, which is essentially an instrument that magnifies the expansion and contraction of a metal under test to such an extent that they are apparent to the unaided eye or can be photographically recorded.

The principle of a dilatometer is illustrated by Fig. 122. The sample *S* is supported in a quartz tube *Q* and a quartz rod transmits any change in the length of the sample to a sensitive dial indicator *G*. The measurements give the differential expansion of the quartz and the sample. From a knowledge of the expansion coefficient of quartz, the expansion of the specimen can be determined. The particular

apparatus illustrated<sup>6</sup> was designed to permit measurements of expansion coefficients from  $-180^{\circ}$  to  $600^{\circ}\text{C}$ . rather than to provide information on high-temperature transformations.

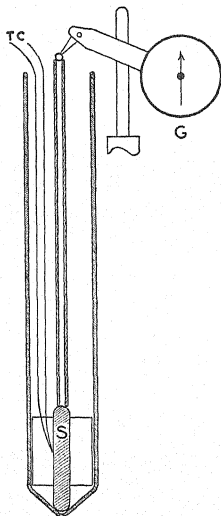


FIG. 122.—Differential dilatometer.

### Summary

For a system in equilibrium  $F = C - P + 2$ . Cooling curves (temperature vs. time) permit detection of phase changes and measurement of specific and latent heats. Inverse rate and differential curves are more sensitive in locating arrests in the cooling. Equilibrium diagrams, constructed from cooling curve data, describe possible equilibrium states of a system, commonly in a two-dimensional

<sup>6</sup> H. Scott, *Trans. Am. Soc. Steel Treating*, 13, 829 (1928).

temperature-composition diagram. Furnaces used to obtain cooling curves should provide control of the cooling rate of the specimen.

### References

- ASTM "Recommended Practice for Thermal Analysis of Steel," *ASTM Standards*, 1936. pp. 806-9.
- Carpenter, H. and Robertson, J. M. *Metals*, London: Oxford U. Press, (2 vol.), 1939.
- International Critical Tables . . .*, New York: McGraw-Hill, 1927, vol. II. pp. 400-455.
- Kehl, G. L. *The Principles of Metallographic Laboratory Practice*, New York, McGraw-Hill, 1939. p. 359.
- Millard, E. B. *Physical Chemistry for Colleges*, New York: McGraw-Hill, 1936. pp. 328-353.

### Problems

1. Gold (m.p. 1063) and thallium (m.p. 300) form no compounds or solid solutions. The eutectic composition is 28% Au, and the eutectic temperature 120°C. Draw a phase diagram, indicating phases present in each field. Draw cooling curves showing the behavior of melts containing 0, 10, 28, and 75% Au.
2. Bismuth (m.p. 271) and tellurium (m.p. 450) form a compound  $\text{Bi}_2\text{Te}_3$  (m.p. 580°C.) containing 48% Te by weight. No solid solutions form. The two eutectic temperatures are 370° and 253° for 15% and 98.8% Bi respectively. Draw an equilibrium diagram and letter its fields. What would happen at 400° if Te were added gradually to Bi, assuming equilibrium to be maintained at all times?

## Elementary Thermodynamics

### Introduction

The science of heat has been seen in earlier chapters to be concerned with properties of matter, changes of state, calorimetry and radiation. It deals also with chemical reactions. The science of heat is studied under the name of thermodynamics, statistical mechanics or kinetic theory. Each implies a different method of approach.

Thermodynamics is primarily the study of energy relations and the direction in which change occurs. It starts by assuming the first and second laws and derives mathematical results from them. Both laws are simple and general. From them are derived the fundamental results of thermodynamics, which are independent of any particular assumptions about atomic and molecular structure or about the exact mechanisms by which energy is exchanged. In spite of simplicity and generality, thermodynamics has the drawback that there are many problems which it simply cannot answer—detailed problems relating, for example, to the equation of state and specific heats of particular substances. Thermodynamics can predict certain relations between observed quantities, but not the values of those quantities. Further, on account of the form of the second law, thermodynamics can give quantitative information only for systems which are in equilibrium.

Statistical mechanics undertakes to answer the question, how is each particle of the substance moving and how do these motions lead to the observable, large-scale phenomena? For example, how do the motions of the molecules of a gas

lead to collisions with a wall which is interpreted as pressure? Statistical mechanics can start with detailed models of matter and then through them predict the results of large-scale experiments. The first and second laws of thermodynamics are derivable from statistical mechanics. Statistical mechanics is more detailed and somewhat more complicated than thermodynamics. Like thermodynamics it is limited to the treatment of problems in equilibrium.

Kinetic theory is a study of the rates of atomic and molecular processes, treated by fairly direct methods, without much benefit of general principles. It is superior to statistical mechanics and thermodynamics in just two respects: it makes use only of well-known, elementary methods, and it can handle problems relating to systems not in equilibrium (such as reaction rates).

### First law of thermodynamics

The law of the conservation of energy, which is the common principle of all physical sciences, is usually expressed somewhat metaphorically by saying that when energy is destroyed in one form, it appears in a corresponding quantity in another form. The steps which established the principle were:

(1) Black's discovery of the latent heat of change of state.

(2) The discovery of the nature of combustion. Crawford, Lavoisier and Laplace showed that animal heat or the heat of a candle flame bears a constant relation to the amount of oxygen, food or wax consumed.

(3) The discovery and measurement of the mechanical equivalent of heat, by Joule (1841) and others.

Contemporaries of Rumford considered heat as a fluid, sometimes called caloric, which was abundant in hot bodies and lacking in cold ones. This theory was adequate for calorimetry, using the assumption that caloric or heat was conserved. This assumption met a critical difficulty in

Rumford's observations on the boring of cannon. Rumford noticed that a great deal of heat was given off in the process of boring. The current explanation of this was that chips of metal had their heat capacities reduced by the process of boring, so that the heat which was originally present in them was able to raise them to a higher temperature. Rumford tested this assumption by using a very blunt tool which removed few chips and yet produced even more heat than a sharp tool. His experiments showed that heat could be produced continuously, and in apparently unlimited quantity, by friction. Surely this was impossible if heat or caloric were a fluid which was conserved. Rumford essentially suggested that the heat was the mechanical energy which had disappeared, observed in a different form. This hypothesis received experimental proof some years later when Joule showed that when a certain amount of work or mechanical energy disappears, the amount of heat appearing is always the same, no matter what the process of transformation may be. Thus the calorie, formerly considered as a unit for measuring the amount of caloric present, was seen to be really a unit of energy, convertible into ergs, the ordinary unit of energy:

$$1 \text{ calorie} = 4.185 \times 10^7 \text{ ergs} = 4.185 \text{ joules}$$

In applying thermodynamic reasoning, the region considered, separated from its surroundings by imaginary boundaries, is called a system. The total energy of all sorts contained within the system is called the internal energy of the system and is denoted by  $U$ . In an infinitesimal change of the system, the energy which enters the system as heat is called  $\delta Q$  and that which leaves the system as mechanical work is called  $\delta W$ . The law of conservation of energy is expressed as

$$\delta U = \delta Q + \delta W \quad (1)$$

Since the formulation of the principle of the conservation of energy about the middle of the nineteenth century, its

validity has been seriously questioned only in atomic phenomena. With the discovery of radioactivity and the heat liberated by the disintegration of the radioactive elements, it was necessary to perform calorimetric experiments to show that energy was conserved even in radioactive processes. More recently it has been found necessary to invent a new fundamental particle, the elusive neutrino, to balance the energy equation in certain atomic processes.

In view of the deference shown the conservation of energy principle, the reader may well ask with Poincaré,<sup>1</sup> “. . . who gives us the right of attributing to the principle itself more generality and more precision than to the experiments which have served to demonstrate it?” Poincaré answers: “We admit it because certain experiments have shown us that it will be convenient, and thus it is explained how experiment has built up the principles of mechanics, and why, moreover, it cannot reverse them . . . Whatever fresh notions of the world may be given us by future experiments, we are certain beforehand that there is something which remains constant, and which may be called energy . . . How then shall we know when it has been extended as far as it is legitimate? Simply when it ceases to be useful to us—i.e., when we can no longer use it to predict correctly new phenomena.”

Some of the extensions of the conservation of energy principle which have been made since its formulation will be discussed in the following paragraphs. In digression, the reader who wishes to know how an apparent failure of the conservation of energy principle would be treated will find it interesting to trace just such a case in the original papers referred to below.<sup>2</sup>

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<sup>1</sup> . . . *Science and Hypothesis* . . . , New York: The Science Press, 1913.

<sup>2</sup> For a summary see T. H. Osgood, *Rev. Sci. Instruments*, **8**, 7 (1937).

R. S. Shankland, *Phys. Rev.*, **49**, 8 (1936); **50**, 571 (1916).

P. A. M. Dirac, *Nature*, **137**, 298 (1936).

E. J. Williams and E. Pickup, *Nature*, **138**, 461 (1936).



The modern study of atomic physics has introduced radically new concepts in physics and has increased knowledge of the manner in which energy transformations occur. The older physics recognized three separate conservation laws, expressing, respectively, the constancy of the mass, the momentum and the energy of an isolated system. Einstein introduced a far-reaching new generalization by postulating the equivalence of mass and energy. "Every quantity of energy of any form whatever represents a mass which is equal to this same energy divided by  $c^2$ , where  $c$  is the velocity of light, and every quantity of energy in motion represents momentum." Expressed as an equation:

$$U = mc^2$$

The older so-called classical physics is unable to explain satisfactorily the observed values of specific heats, the production of spectra, or radiation curves of the sort shown in Fig. 43, Chap. V. In an attempt to discover the laws governing such phenomena, Planck introduced the assumption that the interchange of energy between matter and radiation was not a continuous process. Planck assumed that matter (an aggregate of atoms) could be regarded as a collection of linear oscillators, and that energy could be emitted or absorbed only in multiples of some small energy unit  $\epsilon$ , called a quantum. The magnitude of the energy unit was shown to depend upon the frequency  $\nu$  of the oscillator,

$$\epsilon = h\nu$$

where  $h$  is Planck's action constant, having dimensions erg seconds.

Bohr extended Planck's quantum hypothesis to apply to the radiation emitted by an atom when its internal energy diminished by an amount  $U$

$$U = h\nu$$

The heavier elements may be regarded as built up from hydrogen nuclei and electrons. Measurements with a mass

spectrograph give the weight of a neutral hydrogen atom as 1.008158 atomic weight units. On the same scale the atomic weight of an electron is 0.0054. The atomic weight of a neutral oxygen atom might be expected to be  $16(1.008158) = 16.1305$ . Comparing this with the value 16 used in defining the atomic weight scale, one observes that the building of an oxygen atom results in the disappearance of a mass equal to 0.1305 atomic weight units (or  $2.169 \times 10^{-23}$  gm.). The energy of the system is decreased by an amount which may be calculated from  $U = mc^2$ . This energy is radiated as an electromagnetic wave of definite frequency  $\nu$  and wavelength  $\lambda$ ,

$$U = mc^2 = h\nu = h \frac{c}{\lambda} \quad (2)$$

For the case considered,  $U = 1.9487 \times 10^{-4}$  erg and hence  $\lambda$  may be calculated as  $1.0071 \times 10^{-12}$  cm.

A relationship between different ways of expressing energy, which is convenient to remember, is

$$x \text{ cal.} = 4.185 \text{ erg} = h\nu = h \frac{c}{\lambda} = \frac{1}{300} Ee \quad (3)$$

$E$  is a potential difference measured in volts,  $e$  is the charge of an electron measured in electrostatic units. The term electron volt is frequently used to specify the energy acquired by an electron in moving through a difference of potential of 1 volt.

### Second law of thermodynamics

The second law of thermodynamics is concerned with the direction in which energy transfers occur. It expresses the fact that heat will not of its own accord flow from a body of lower temperature to one of higher temperature. To clarify the meaning of "of its own accord," the second law is stated: no self-acting engine can transfer heat from a body of lower temperature to one of higher temperature.

A self-acting engine is one on which no external work is done and which operates in such a manner as to take the working substance through one or more complete cycles. Other definitions needed for a discussion of the second law follow.

A reversible transformation is one which can be made to occur in the opposite sense by an infinitesimal change

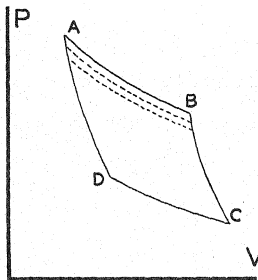


FIG. 123.—Carnot cycles.

in any one of the conditions determining the transformation. If, for example, a gas is expanding reversibly, an infinitesimal increase in the pressure to which it is subjected will cause it to contract. Clearly a reversible transformation must take place very slowly. During such a transformation the different parts of the system are infinitesimally close to thermal equilibrium at every instant.

An isothermal transformation is one during which the temperature remains constant.

An adiabatic transformation is one during which heat is neither gained nor lost.

A cycle is a succession of transformations which brings the working substance back to its initial state.

A Carnot cycle is a cycle consisting of two isothermal and two adiabatic transformations. It may be represented on a pressure-volume diagram by the curve *abcd* of Fig. 123. The cycle could be realized, ideally, by using as the working substance a gas confined by an insulated cylinder and piston (Fig. 124). The steps would be:

*ab* Cylinder in thermal contact with hot reservoir  $T_1$ . Gas expanded isothermally, taking in heat.

- bc* Cylinder insulated. Gas expanded adiabatically.  
*cd* Cylinder in thermal contact with low-temperature reservoir  $T_2$ . Gas compressed isothermally, giving heat to the reservoir.  
*da* Cylinder insulated. Compression continued adiabatically until gas is restored to its original state.

The efficiency of a heat engine is the ratio of the work done by the engine in a complete cycle to the heat taken in.

Two theorems based on the second law of thermodynamics will now be proved.

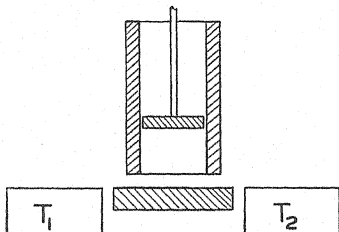


FIG. 124.—Carnot engine.

*Theorem I.* No heat engine can have a greater efficiency than a reversible engine working between the same temperatures. Consider that in Fig. 125 an irreversible engine  $E'$  is driving a reversible engine  $E$  backwards. The heat quantities transferred between the high-temperature reservoir  $T_1$  and the low-temperature reservoir  $T_2$  are indicated. As  $E$  is reversible the heat  $Q_1$  which it gives to  $T_1$  per cycle equals the amount of heat it would take from  $T_1$  if it were running in the forward sense. Similar statements are true of  $Q_2$  and the work  $W$  done on  $E$  per cycle. Therefore the efficiencies of the two engines are

$$E = \frac{W}{Q_1} \quad \text{and} \quad E' = \frac{W'}{Q_1'}$$

The work  $W'$  done by  $E'$  per cycle is the work  $W$  done on  $E$ . Therefore

$$Q_1 - Q_2 = Q_1' - Q_2' \quad (4)$$

from the first law of thermodynamics, and

$$EQ_1 = E'Q_1' \quad (5)$$

from the expressions for the efficiencies.

Suppose that, contrary to the theorem being proved,  $E' > E$ . Then  $Q_1 > Q_1'$  from Eq. 5 and  $Q_2 > Q_2'$  from

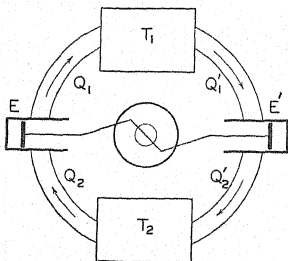


FIG. 125.—Connected pair of heat engines.

Eq. 4. The result would be that the two engines constituting together a self-acting engine would transfer heat from the refrigerator  $T_2$  to the hot reservoir  $T_1$ . But this is a contradiction of the second law of thermodynamics. Hence we conclude

$$E' \leq E \quad (6)$$

*Theorem II.* All reversible engines working between the same two temperatures have the same efficiency, irrespective of working substance. Consider two reversible engines of efficiencies  $E_1$  and  $E_2$  which use different working substances. Either one may take the place of  $E$  in the previous discussion, the other being operated in reverse. Therefore  $E_1 \leq E_2$

and  $E_2 \leq E_1$  must be satisfied, giving

$$E_1 = E_2 \quad (7)$$

### Kelvin absolute temperature scale

Carnot's principle provides a way of defining a scale of temperature which is independent of the thermometric substance. Imagine a hundred reversible engines all of which run through Carnot cycles of the same area on the pressure-volume diagram. Let the first engine receive heat at the temperature of boiling water, the second receive the heat rejected by the first and so forth. If the size of the cycle is properly adjusted, the last engine may be made to discharge heat at the temperature of melting ice. By assigning the values  $100^\circ$ ,  $99^\circ$ ,  $98^\circ$ , . . .  $0^\circ$  to the temperatures represented by the isothermals in Fig. 123, we have defined the centigrade absolute temperature scale in a manner independent of the working substance used. A second set of a hundred reversible engines using a different working substance would determine the same temperatures since reversible engines operating between the same two temperatures have the same efficiency.

The centigrade absolute scale may be extended above  $100^\circ\text{C}$ . and below  $0^\circ\text{C}$ . by continuation of the procedure indicated above. The temperature at which the last engine in the series would discharge no heat may be interpreted at the absolute zero on the temperature scale.

It may be shown that the heat  $Q_1$  taken in by an engine during an isothermal transformation  $ab$  (at temperature  $T_1$ ) is represented by the area under the curve. Similarly if the engine rejects heat at temperature  $T_2$ , the heat rejected is represented by the area under the  $T_2$  isothermal. Hence the useful work done by the engine is proportional to the temperature difference

$$W = Q_1 - Q_2 = k(T_1 - T_2)$$

If the engine rejected no heat to the sink

$$Q_2 = 0 = k(T_2 - 0)$$

By combining the last two equations, the efficiency of the engine is given by

$$E = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (8)$$

It follows that the ratio of the heat taken in to that rejected is equal to the ratio of the corresponding absolute temperatures

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (9)$$

The thermodynamic temperature scale has been defined in terms of an idealized experiment. The importance of the mental experiment here described is that temperatures so defined are independent of the nature of the working substance.

### Entropy and the second law

To facilitate a mathematical statement of the second law of thermodynamics it is convenient to introduce the idea of entropy. The increase of entropy  $dS$  occurring when an amount of heat  $\delta Q$  is absorbed in a reversible transformation is given by  $dS = \delta Q/T$ . The entropy is a quantity characteristic of the state of the system. If a system passes from one state to another in a reversible way,  $\int \delta Q/T$  proves to be an integral whose value is independent of the path. It gives the difference in entropy between the two states. The same integral evaluated from an arbitrary zero point (usually taken as the absolute zero of temperature) gives the entropy of a state. To calculate the change in entropy for an irreversible process it is necessary to replace the irreversible process by a reversible transformation connecting the same two terminal states. Then  $\int \delta Q/T$  applied to the reversible transformation gives the desired change in entropy.

The second law may now be stated in a mathematical form as

$$dS = \frac{\delta Q}{T} \text{ for a reversible process}$$

$$dS > \frac{\delta Q}{T} \text{ for an irreversible process} \quad (10)$$

Combining this with the first law we get

$$TdS \geq dU + \delta W \quad (11)$$

in which, for reversible processes the equality sign is used. Clausius summed up the first and second laws of thermodynamics, respectively, by saying that *the energy of the world remains constant* and that *the entropy of the world tends to a maximum*.

In describing the state of a substance we may choose any two of the five variables  $u$ ,  $s$ ,  $T$ ,  $v$ , and  $p$  as independent variables, expressing the remaining three as functions of these.  $du$ ,  $ds$  and  $dT$  are exact differentials in  $dp$  and  $dv$ , while  $\delta q$  and  $\delta w$  are not exact. The integrals  $\int \delta q$  and  $\int \delta w$  are not independent of path, which is only another way of saying that mechanical and heat energy are interchangeable.

### Common thermodynamic coefficients

When one of the five variables,  $p$ ,  $v$ ,  $T$ ,  $u$  and  $s$ , is differentiated with respect to another it is necessary to specify the second independent variable, the one which is held constant in the differentiation. It is convenient to indicate this by a subscript. Thus  $(\partial v / \partial T)_p$  is the derivative of  $V$  in which  $T$  and  $p$  are independent variables. There are a number of partial derivatives whose meanings are already familiar,

$$\frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \alpha_p = \text{coefficient of thermal expansion at constant pressure}$$

$$\frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_v = \alpha_v = \text{coefficient of change of pressure at constant volume}$$



$-\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$  = isothermal compressibility (reciprocal of modulus of elasticity for isothermal change,  $M_t$ )

$-\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_s$  = adiabatic compressibility (reciprocal of modulus of elasticity for adiabatic change,  $M_s$ )

$\left( \frac{\partial u}{\partial T} \right)_v = T \left( \frac{\partial s}{\partial T} \right)_v = C_v$  = heat capacity at constant volume

To find the heat capacity at constant pressure,  $C_p$ , Eq. 11 is written in the form

$$Tds = du + pdv \quad (12)$$

Then  $C_p$ , the heat absorbed divided by the change in temperature at constant pressure, becomes

$$C_p = T \left( \frac{\partial s}{\partial T} \right)_p = \left( \frac{\partial u}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p \quad (13)$$

### Common thermodynamic functions

Several function of the thermodynamic variables appear frequently in thermodynamic calculations and have been given various names. They are defined by the following equations

$H = U + PV$  Heat content. Enthalpy. Gibbs'  $\chi$  function.

$A = U - TS$  Helmholtz free energy. Gibbs'  $\psi$  function.

$G = H - TS = U - TS + PV$  Gibbs free energy. Gibbs'  $\zeta$  function.

### Methods of deriving thermodynamic relations

In view of the large number of partial derivatives which can be formed from the thermodynamic variables, it is advantageous to have a systematic procedure for finding any

particular formula that may be needed. The four mathematical methods of finding thermodynamic formulas are summarized in the following.

(1) Eq. 12 and other thermodynamic relations are of the form

$$dx = K dy + L dz \quad (14)$$

where  $K$  and  $L$  are functions of the variables. Additional formulas are obtained from such an expression by dividing by the differential of one variable, say  $du$ , and indicating that the process is for a constant value of another, say  $w$ ,

$$\left(\frac{\partial x}{\partial u}\right)_w = K \left(\frac{\partial y}{\partial u}\right)_w + L \left(\frac{\partial z}{\partial u}\right)_w \quad (15)$$

Only when  $dx$  is the differential of a function of the state of the system is it proper to write partial derivatives like  $(\partial x / \partial u)_w$ . Corresponding expressions could not be written, for example, using  $\delta W$  or  $\delta Q$ . Since  $(\partial x / \partial y)_z = K$  and  $(\partial x / \partial z)_y = L$ , Eq. 15 may be written

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (16)$$

which is the familiar mathematical equation expressing a total differential  $dx$  in terms of partial derivatives.

(2) For ordinary derivatives,  $\frac{dx/du}{dy/du} = \frac{dx}{dy}$ . Hence two partial derivatives taken with respect to the same variable and with the same variable held constant are related by

$$\frac{(\partial x / \partial u)_z}{(\partial y / \partial u)_z} = \left(\frac{\partial x}{\partial y}\right)_z \quad (17)$$

(3) If  $x$  is constant in Eq. 16,  $dx = 0$ , and the equation may be solved for  $dy/dz$  which will be  $(\partial y / \partial z)_x$

$$\left(\frac{\partial y}{\partial z}\right)_x = - \frac{(\partial x / \partial z)_y}{(\partial x / \partial y)_z} \quad (18)$$

Using Eq. 17 this equation may be rewritten in either of the two forms

$$\left(\frac{\partial y}{\partial z}\right)_x = -\frac{(\partial y / \partial x)_z}{(\partial z / \partial x)_y}, \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (19)$$

(4) The fundamental theorem regarding second partial derivatives

$$\left[\frac{\partial}{\partial z} \left(\frac{\partial x}{\partial y}\right)_z\right]_y = \left[\frac{\partial}{\partial y} \left(\frac{\partial x}{\partial z}\right)_y\right]_z$$

when applied to Eq. 14 makes

$$\left(\frac{\partial K}{\partial z}\right)_y = \left(\frac{\partial L}{\partial y}\right)_z \quad (20)$$

Four important relations result from applying Eq. 20 to the differential expression of the first and second laws, Eq. 12. These are

$$\left. \begin{aligned} -\left(\frac{\partial T}{\partial v}\right)_s &= \left(\frac{\partial p}{\partial s}\right)_v \\ \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_v \\ \left(\frac{\partial T}{\partial p}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_p \\ -\left(\frac{\partial s}{\partial p}\right)_T &= \left(\frac{\partial v}{\partial T}\right)_p \end{aligned} \right\} \quad (21)$$

Equations 21 are generally called Maxwell's relations.

Any desired relation connecting the first derivatives of the thermodynamic variables may be derived by applying the four processes just considered, or combinations of them. Such formulas have been classified and tabulated for convenience in use.<sup>3</sup>

<sup>3</sup> P. W. Bridgman, *A Condensed Collection of Thermodynamic Formulas*, Harvard U. Press.

J. C. Slater, *Introduction to Chemical Physics*, McGraw-Hill, 1939. pp. 27-29.

**Joule-Thomson effect**

The Joule-Thomson porous-plug experiment consists in measuring the cooling experienced by a gas flowing through a porous plug 0 from a region of pressure  $p_1$  to a region of lower pressure  $p_2$  in a thermally insulated chamber (Fig. 137, Chap. XIV). It is important because it provides a way of calculating absolute thermodynamic temperatures from measurements and corrections obtained with a constant pressure thermometer using a real gas.

The net work done by a unit mass of gas in passing through the plug is  $\delta w = p_2 v_2 - p_1 v_1 = d(pv)$ . As no heat is taken in  $d(u + pv) = dH$

$$\delta q = du + \delta w = du + d(pv) = d\chi = 0$$

since

$$du + pdv = Tds$$

we have

$$Tds + vdp = 0$$

or

$$T \left( \frac{\partial s}{\partial T} \right)_p dT + T \left( \frac{\partial s}{\partial p} \right)_T dp + vdp = 0$$

Now

$$T \left( \frac{\partial s}{\partial T} \right)_p = c_p, \quad \left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p$$

Hence

$$c_p dT = \left( T \frac{\partial v}{\partial T} - v \right) dp$$

or

$$\left( \frac{\partial T}{\partial p} \right)_H = \frac{T(\partial v / \partial T)_p - v}{c_p} \quad (22)$$

This gives the differential Joule-Thomson effect  $(dT/dp)_H$ . Eq. 22 may be written

$$c_p \left( \frac{dT}{dp} \right)_H = T \left( \frac{\partial v}{\partial T} \right)_p - v = -T \left( \frac{\partial p}{\partial T} \right)_v - v$$

Comparing with Eq. 12, it follows that

$$c_p \left( \frac{dT}{dp} \right)_u = - \left( \frac{\partial H}{\partial p} \right)_T = - \left( \frac{\partial u}{\partial p} \right)_T - \left( \frac{\partial(pv)}{\partial p} \right)_T \quad (23)$$

The first term on the right measures the deviation of the gas from Joule's law  $[(\partial u / \partial v)_T = 0]$  while the second gives the deviation from Boyle's law  $[pv = f(T)]$ . The Joule-Thomson effect is the resultant of deviations from both these laws. That part of the internal energy which is due to molecular attraction always decreases with decrease of volume (i.e., with increase of pressure) so  $(\partial u / \partial p)_T$  is negative. Hence due to deviation from Joule's law alone the Joule-Thomson effect is a cooling effect. Superposed on this is the effect due to deviation from Boyle's law, which is a cooling or heating effect depending on whether  $\frac{\partial(pv)}{\partial p}$  is negative or positive.

### Joule-Thomson effect for a Van der Waal's gas

For a perfect gas, the right hand side of Eq. 23 is easily seen to be zero and hence the Joule-Thomson effect vanishes. For a gram molecule of gas obeying a Van der Waal equation of state,  $\left( p + \frac{a}{V^2} \right) (V - b) = RT$ , it can be proved that

$$\begin{aligned} \left( \frac{\partial T}{\partial p} \right)_u &= \frac{2a(V-b)^2 - bV^2RT}{RTV^3 - 2a(V-b)^2} \frac{V}{C_p} \\ &= \frac{1}{C_p} \frac{\frac{2a}{R} \left( 1 - \frac{b}{V} \right)^2 - b}{1 - \frac{2a}{RTV} \left( 1 - \frac{b}{V} \right)^2} \\ &\doteq \frac{1}{c_p} \left[ \frac{2a}{RT} - b \right], \text{ neglecting } \frac{b}{V} \text{ and } \frac{2a}{RTV} \end{aligned}$$

Hence cooling accompanies a decrease in pressure as long as  $T < 2a/bR$ . The temperature given by  $T_i = 2a/bR$  is called the inversion temperature, since on passing this temperature the Joule-Thomson effect changes sign. The critical tem-

perature and pressure for a gas obeying Van der Waal's law are found by setting both  $\partial p / \partial v$  and  $\partial^2 p / \partial v^2$  equal to zero. They are:  $T_c = 8a / 27Rb$  and  $p_c = a / 27b^2$ , or  $RT_c / p_c v_c = 8/3$ . The inversion temperature is seen to be approximately  $27/4 T_c$ .

### Correction of gas thermometer

Eq. 22 can be utilized to give the absolute thermodynamic temperatures from observations on an ordinary gas thermometer. If  $\theta$  and  $C_p'$  are used to represent temperature and specific heat measured on an arbitrary gas thermometer scale,

$$C_p = \frac{dQ}{dT} = \frac{dQ}{d\theta} \frac{d\theta}{dT} = C_p' \frac{d\theta}{dT}$$

$$\left( \frac{\partial T}{\partial p} \right)_n = \frac{dT}{d\theta} \left( \frac{\partial \theta}{\partial p} \right)_n$$

hence

$$C_p \left( \frac{\partial T}{\partial p} \right)_n = C_p' \left( \frac{\partial \theta}{\partial p} \right)_n$$

also

$$\left( \frac{\partial v}{\partial T} \right)_p = \left( \frac{\partial v}{\partial \theta} \right)_p \frac{d\theta}{dT}$$

so Eq. 22 yields

$$\int_{T_1}^{T_2} \frac{dT}{T} = \int_{\theta_1}^{\theta_2} \frac{(\partial v / \partial \theta)_p d\theta}{v + C_p (\partial \theta / \partial p)_n} \quad (24)$$

The quantity on the right can be measured on any thermometer, the same thermometer being used for all measurements. If their dependence on  $\theta$  is known from experiment the integration can be performed. Assuming this to be done, and taking  $\theta_1$  and  $\theta_2$  to refer to the temperature of melting ice and condensing steam, respectively,

$$\log_e \frac{T_{100}}{T_0} = \log_e \frac{T_0 + 100}{T_0} = X$$

where  $X$  is the value of the integral (Eq. 24) between the

limits  $0^\circ$  and  $100^\circ$ , since by definition  $T_{100} - T_0 = 100$ . This determines  $T_0$ . Any other temperature  $T_1$  can be found from the relation

$$\log_e \frac{T_1}{T_0} = \int_0^{\theta_1} \frac{(\partial v / \partial \theta)_p d\theta}{v + C_p' (\partial \theta / \partial p)_n} \quad (25)$$

In general there are not sufficient data to give accurately the variation of the Joule-Thomson effect with temperature. In such cases a practical procedure is to write the equation of state for the gas from what ever experimental data are available. The equation is usually expressed in the form<sup>4</sup>

$$pV = A + Bp + Cp^2 + Dp^3 + \dots \quad (26)$$

The constants  $A$ ,  $B$ ,  $C$ , and  $D$  are complicated functions of the temperature, but are independent of pressure. They are found by noting the volume occupied by the gas at different pressures. Experiments<sup>5</sup> on a number of gases in the range from  $-183^\circ$  to  $400^\circ\text{C}$ . have shown that the  $D$ -term and those following are negligible. Thus the equation simplifies to  $pV = A + Bp$ . It is easily seen that for low density ( $p \rightarrow 0$ ) the gas obeys Boyle's law ( $pV = A$ ), that is, it behaves like a perfect gas. Hence in order to obtain temperature readings corrected to an ideal gas scale, observations are made on a real gas and the results extrapolated to  $p \rightarrow 0$ .

### Summary

Gases which deviate from the ideal laws of Joule and Boyle experience a Joule-Thomson effect, i.e., a heating or cooling when expanded adiabatically through a porous plug. The Joule-Thomson effect is of theoretical importance in permitting calculation of thermodynamic temperatures from measurements with a gas thermometer, and of practical importance in the commercial liquefaction of gases.

<sup>4</sup> K. Onnes, *Commun. Phys. Lab. Univ. Leiden*, No. 71 (1901).

J. Otto, *Hand. Exp. Physik*, 8, part 2, 191 (1929).

<sup>5</sup> L. Holborn and J. Otto, *Z. Physik*, 33, 9 (1925).

The interchangeability of heat and mechanical energy is expressed in the first law of thermodynamics:

$$\delta U = \delta Q + \delta W.$$

The conservation principle has been extended to include interchange of mass and energy:  $U = mc^2$ . The second law of thermodynamics is concerned with the direction in which energy transfers occur. It is given mathematical expression by introducing the concept of entropy:  $dS = \delta Q/T$  (reversible process);  $dS > \delta Q/T$  (irreversible process). The first and second laws may be combined in the expression:  $TdS \geq dU + \delta W$ .

### References

- Slater, J. C. *Introduction to Chemical Physics*, New York: McGraw-Hill, 1939.
- Zemansky, M. W. *Heat and Thermodynamics*, New York: McGraw-Hill, 1937.

### Problems

1. What is the thermodynamic efficiency of a non-condensing steam engine which uses steam at a pressure of 150 lb./in.<sup>2</sup> (saturation temperature 358.43°F.)?
2. What advantage results from using mercury vapor instead of steam in driving turbines?
3. An ideal engine has an efficiency of 25 per cent when its condenser temperature is 25°C. What change in (i) condenser temperature or (ii) boiler temperature would be necessary to increase the efficiency to 35 per cent?
4. Compare the heating effects produced in a room at 17°C. by a given quantity of electrical energy, (i) if the electrical power is dissipated in a resistance heater, and (ii) if the electrical power is used to operate an ideal heat engine to transfer heat from the outside (-5°C.) to the room. Comment on the practical possibility of such a scheme.
5. List in outline form the steps necessary in defining the thermodynamic (Kelvin) temperature scale.
6. State clearly how the reading of a laboratory temperature indicator would be converted into the corresponding absolute temperature in



- the neighborhood of (i)  $-200^{\circ}\text{C.}$ , (ii)  $20^{\circ}\text{C.}$ , (iii)  $500^{\circ}\text{C.}$ , (iv)  $1500^{\circ}\text{C.}$ ?
7. What energy, measured in electron volts, is necessary to excite the 2536.5Å resonance line in mercury vapor?
  8. It requires 4.42 v. to dissociate  $\text{H}_2$  into  $\text{H} + \text{H}$ . Calculate the heat of formation of  $\text{H}_2$  in cal./gm.
  9. If an atom of oxygen (at. wt. 16.00000) were built up of hydrogen atoms (at. wt. 1.00778) and electrons in one step, what frequency of radiation should be associated with the process?
  10. What is the change in entropy of 10 gm. of ice when sufficient heat is added to melt it?
  11. A mercury thermometer has been heated until the mercury just fills the bore. If the temperature is further increased by  $1^{\circ}\text{C.}$ , what will be the internal pressure? (Coefficient of compression for mercury is  $3.9 \times 10^{-6}$  per atm.)
  12. Show that if the thermal capacity  $c$  of a solid remains constant, the change in entropy  $\Delta S$  in heating  $M$  gm. of it from  $T_0$  to  $T$  is  $Mc \log_e \frac{T}{T_0}$ .
  13. Show that if the specific heats of a gas remain constant and if as heat is added to the gas it is allowed to expand,

$$\frac{\Delta S}{M} = c_v \log_e \frac{T_2}{T_1} + nR \log_e \frac{V_2}{V_1}.$$

## CHAPTER XIII

# Special Methods of Temperature Measurement

### Determination of gas temperatures

The temperature of a gas placed in an isothermal enclosure can be measured with no difficulty. Any measuring device placed in the gas attains the equilibrium temperature and indicates correctly the temperature of the gas.

In problems of practical interest, however, the gas temperature is often quite different from that of its surroundings and any pyrometer measurements made in the gas without suitable precautions are liable to large errors. The desirability of shielding the thermometer from radiation and of increasing the heat transfer from gas to thermometer by forced convection has long been recognized in the design of the aspiration thermometers used for meteorological measurements.

Gas temperature measurements are of considerable industrial importance in the control of boiler furnaces, heat exchangers, glass furnaces, etc. An outline of the principal methods and precautions used may suggest designs for particular applications.<sup>1</sup>

(i) *Radiation protecting shield.* If a stream of gas at temperature  $T$  is passing through a tube whose walls are at a lower temperature  $T_w$ , a pyrometer placed in the gas assumes a temperature  $T_p$  intermediate to  $T_w$  and  $T$ . If  $a$  is the coefficient for energy exchange by conduction and convection

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<sup>1</sup> For a bibliography (130 references) see H. F. Mullikin, "Gas Temperature Measurements and the High Velocity Thermocouple." *Temperature—Its Measurement and Control* . . . , New York: Reinhold, 1941. pp. 775-804.

between the pyrometer and the gas, and  $b$  is the radiation coefficient, one can write for unit area

$$a(T - T_p) = b(T_p^4 - T_w^4). \quad (1)$$

If a shield  $S_1$  (Fig. 126) is interposed between the pyrometer and the wall, it will assume a temperature  $T_1$  lower than  $T$  but higher than  $T_w$ . The equation for thermal equilibrium then becomes

$$a(T - T_p') = b(T_p'^4 - T_1^4) \quad (2)$$

where  $T_p'$  is the new temperature of the pyrometer. Since  $T_1^4$  is much greater than  $T_w^4$ ,  $T_p'$  is greater than  $T_p$  and the accuracy of the pyrometer indication is improved. A second

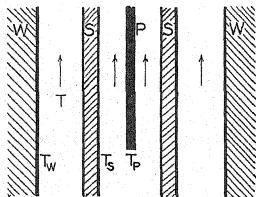


FIG. 126.—Radiation shields for a pyrometer.

shield  $S_2$  may be added to make  $T_p''$  approach more nearly the true gas temperature. But unless the gas velocity through the shields is appreciable, considerable error remains.

(ii) *Thermocouples with different diameters.* The radiation error of a thermocouple decreases as the diameter of the wire is made smaller. Because of the existence of a gas film, the effective area receiving heat by convection is larger than the actual surface of the wire losing heat by radiation. The use of very small thermocouples is impractical because of their fragility. However, if measurements are made with a number of thermocouples of different diameters, a curve of indicated temperature against wire diameter may be drawn and extrapolated to zero diameter to obtain an estimate of the gas temperature.

(iii) *Radiation, optical or color pyrometers* are subject to large errors when used to indicate gas temperatures directly. They generally measure a surface temperature. Their readings require corrections, usually unknown, for emissivity and for thickness of the gas layer.

(iv) *High velocity thermocouple.* A thermocouple using a radiation shield and forced convection appears to be the most satisfactory method of measuring gas temperatures in many industrial applications. Figure 127 shows a pyrometer of this design for measuring temperature in slag-bearing gases up to 3100°F. The gases are drawn through a water-cooled

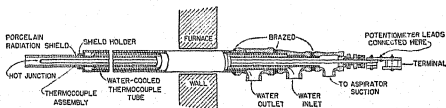


FIG. 127.—Water-cooled high-velocity aradiant thermocouple.

tube by means of an aspirator operating by compressed air. At the furnace end, a thermocouple hot junction surrounded by a porcelain radiation shield is heated by the high velocity gases flowing past, thus giving the gas temperature. The construction facilitates replacement of the shield or the thermocouple junction when the instrument becomes plugged

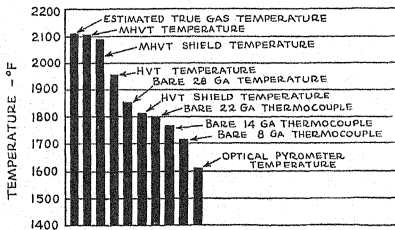


FIG. 128.—Gas temperature measured by various pyrometers.

or damaged by slag. Similar instruments have been variously called suction, aspiration and aradiant convection pyrometers. It is obvious that the principles of this type of pyrometer can be used with temperature-indicating instruments other than thermocouples. Figure 128 shows the gas temperatures indicated in a certain test by an optical pyrometer, various

bare thermocouples, a high velocity thermocouple and a high velocity thermocouple with multiple shields. Such a comparison is an example of the misinformation supplied by even good instruments when used under conditions other than that for which they were calibrated.

(v) *Heated-shield high velocity thermocouple.* Consider the two shields of Fig. 126 to be co-axial alundum tubes, the outer one provided with a heating coil. When the gas is aspirated through the tubes, the heating of  $S_2$  is varied until its temperature  $T_2$  (read on an auxiliary thermocouple) is equal to the temperature  $T_p$  indicated by the pyrometer. The temperature  $T_p$  is then taken as an accurate indication of the gas temperature, since there is no net radiation from the pyrometer.

(vi) *Resistance thermometers, glass thermometers and expansion thermometers* are usually limited to measuring gas temperatures below  $500^\circ\text{C}$ . They are usually less accurate than thermocouples and more difficult to install.

(vii) *Dynamic gas thermometers.* The rate of flow of gas through an orifice varies as the square root of its absolute temperature.

(viii) *Calorimetric method.* The initial temperature of a gas is calculated by measuring the heat content of a sample. The method is difficult and slow.

(ix) *Gas temperature from velocity of sound.* The fact that the velocity of sound varies as the square root of the absolute temperature of a gas offers an attractive but little-used method of measuring gas temperature.

(x) *Interference and photography* provide methods of measuring gas temperature which are described below.

### Flame temperatures

The temperature of a flame may be defined and measured as the temperature of a solid body which is in thermal equilibrium with it. In using a thermocouple or a resistance thermometer to measure a flame temperature directly, one

encounters the same sort of difficulties as outlined under gas temperature measurements. A method which does not disturb conditions in the flame and which takes account of radiation losses from the measuring element is to be preferred.

One useful method of measuring flame temperature makes use of a wire, heated electrically, which is placed in the flame.<sup>2</sup> It loses heat by radiation, by conduction to its supports and by convection to the surrounding gas. If the wire is at the temperature of the gas, no convection loss occurs, all the heat lost is radiated or convected. Similar conditions prevail if the wire is placed in a vacuum. If the point is found (from a graph) at which both the current and the temperature are the same for the wire in the flame as in a vacuum, then that temperature is the temperature of the

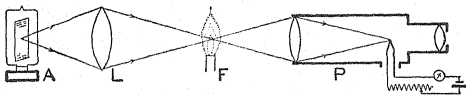


FIG. 129.—Optical measurement of flame temperature, Kurlbaum's method.

flame. The temperature of the wire is determined with a thermocouple or with an optical pyrometer.

If the gases which comprise a luminous flame are in chemical equilibrium at the temperature of the flame and are the only source of radiation (assumptions which are not always justified) then Kirchhoff's law may be applied to measure the flame temperature by an optical method. Light from an auxiliary source  $A$  (an incandescent tungsten foil, an arc or a blackbody) is directed through the flame and on the objective of an optical pyrometer  $P$ , Fig. 129. The brightness observed in the pyrometer is the brightness  $b_{\lambda T}$  of the flame at temperature  $T$  and in addition the brightness of the auxiliary source at temperature  $T'$  which is transmitted by the flame,  $B_{\lambda T'}(1 - \alpha_{\lambda})$ . This will be equal to

<sup>2</sup> E. Griffiths and J. H. Awberry, *Proc. Roy. Soc.*, 123, 401 (1920).

the brightness of the auxiliary source  $B_{\lambda T'}$  alone, provided  $b_{\lambda T} = B_{\lambda T'}\alpha_{\lambda}$ , that is if  $T' = T$ . Observations are made by regulating the auxiliary source until the indication of the optical pyrometer does not change when the flame is interposed. The reading of the optical pyrometer then gives the flame temperature.

The method of spectral line reversal is widely used for measuring temperatures of non-luminous flames. A lens  $L_1$  (Fig. 130) forms an image of an auxiliary light source  $A$  in the flame. A second lens  $L_2$  projects the image of the source and the flame on the slit  $S$  of a spectroscope. The flame is colored by the addition of a small amount of a metallic salt (usually sodium) which furnishes radiation of wavelength  $\lambda$ . If  $B_{\lambda}$  is the spectral brightness of the source  $A$  and  $b_{\lambda}$  is

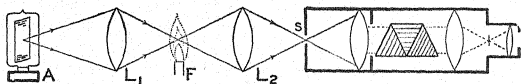


FIG. 130.—Flame temperature by Fery's Na-line reversal method.

the spectral brightness of the flame, the image seen in the spectroscope has a brightness  $B_{\lambda} + b_{\lambda}(1 - \alpha_{\lambda})$ . The brightness matches that of the continuous background illumination from  $A$  provided  $B_{\lambda}/\alpha_{\lambda} = b_{\lambda}$ . From Kirchhoff's law,  $B_{T\lambda}/\alpha_{\lambda}$  represents the brightness of a blackbody at the temperature of the radiating particles. Hence the flame temperature is determined by adjusting  $A$  until the sodium line matches the background illumination, and then measuring the temperature of  $A$  with an optical pyrometer.

The sodium line reversal method has been extensively applied to measuring internal combustion engine temperatures.<sup>3</sup> A quartz window is placed in the cylinder and a stroboscopic shutter permits temperature measurements to be made during any desired part of the operating cycle.

<sup>3</sup> Watts and Lloyd, *Engineering*, 139, 195 (1935); 140, 232 (1935).

W. T. David, *Phil. Mag.*, 21, 280 (1936); 23, 345 (1937); *Nature*, 139, 67 (1937).

### Pyrometric cones

Pyrometric "cones" are slender trihedral pyramids made from mixtures of china clay, feldspar, whiting, flint and fluxes, which by their softening and deformation indicate the heat treatment to which they have been subjected. The cones are particularly useful guides to the proper firing of ceramic products since they behave thermochemically much like the ware. The term "pyrometric cone equivalent" (*PCE*) is used to designate the temperature (strictly, the heat treatment) indicated by pyrometric cones.

Pyrometric cones were made for private use by Lauth and Vogt at the Sevres Pottery in 1882. They were made commercially over an extended temperature range by Seger in 1886. The cone series has subsequently been extended to indicate temperature over a range of from 600 to 2000°C. in intervals of about 20°C.<sup>4</sup> Table I lists a series of standard cones.<sup>5</sup>

Cones are mounted on a plaque at a slight inclination, with the aid of a template, 8° from the vertical being taken as the standard. They are so placed in the kiln as to be subject to a representative heat condition, and are protected from flame or radiation from surfaces markedly hotter than the rest of the kiln. Reducing or sulphurous atmospheres have a detrimental effect on the proper deformation of some cones.

Cones are not pyrometers, and should not be so used. Through the use of radiation pyrometers and modern automatic control, an increasing number of ceramic furnaces are now being held within temperature limits which were not feasible as long as the cone was the only practical method of measuring temperature. Cones, however, measure the

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<sup>4</sup> C. O. Fairchild and M. F. Peters, *J. Am. Ceram. Soc.* 9, [11] 701 (1926).

R. F. Rea, *J. Am. Ceram. Soc.* 21, 98 (1938).

<sup>5</sup> The Edward Orton Jr. Ceramic Foundation, . . . *Pyrometric Cones*, 1937.



maturity of the ware in an accurate manner and in a way that can be compared from plant to plant.

### Thermocolors

Temperature-sensitive paints indicate, by a change of color, when the temperature of the surface has exceeded a

TABLE I  
TEMPERATURE EQUIVALENTS OF CONES<sup>5</sup>  
The Soft Series

Cone number	When fired slowly 20°C. per hour		When fired rapidly 150°C. per hour	
	° Cent.	° Fahr.	° Cent.	° Fahr.
022	585	1085	605	1121
021	595	1103	615	1139
020	625	1157	650	1202
019	630	1166	660	1220
018	670	1238	720	1328
017	720	1328	770	1418
016	735	1355	795	1463
015	770	1418	805	1481
014	795	1463	830	1526
013	825	1517	860	1580
012	840	1544	875	1607
011	875	1607	905	1661

The Low Temperature Series

010	890	1634	895	1643
09	930	1700	930	1706
08	945	1733	950	1742
07	975	1787	990	1814
06	1005	1841	1015	1859
05	1030	1886	1040	1904
04	1050	1922	1060	1940
03	1080	1976	1115	2039
02	1095	2003	1125	2057
01	1110	2030	1145	2093
1	1125	2057	1160	2120
2	1135	2075	1165	2129
3	1145	2093	1170	2138
4	1165	2129	1190	2174
5	1180	2156	1205	2201
6	1190	2174	1250	2282
7	1210	2210	1260	2300
8	1225	2237	1285	2355
9	1250	2282	1305	2381
10	1260	2300	1325	2417
11	1285	2345	1335	2435
12	1310	2390	1350	2462
13	1350	2462	1400	2552
14	1390	2534	1435	2615
15	1410	2570	1465	2669
16	1450	2642	1475	2687
17	1465	2669	1490	2714
18	1485	2705	1520	2768
19	1515	2759	1530	2786
20	1520	2768		

<sup>5</sup>The Edward Orton Jr. Ceramic Foundation, . . . *Pyrometric Cones*, 1937.

TABLE I.—(Continued)  
The High Temperature Series

Cone number	When heated at 100° per hour	
	° Cent.	° Fahr.
23	1580	2876
26	1595	2903
27	1605	2921
28	1615	2939
29	1640	2984
30	1650	3002
31	1680	3056
32	1700	3092
32½	1725	3137
33	1745	3173
34	1760	3200
35	1785	3245
36	1810	3290
37	1820	3308
38	1835	3335
*39	1865	3389
40	1885	3425
41	1970	3578
42	2015	3659

\* The last four cones were heated 600° per hour.

predetermined value. This chemical method of temperature measurement has certain obvious advantages over more exact physical methods. It gives information about an entire surface at a glance. Indications are independent of the distance. It provides a simple and inexpensive way of safeguarding bearings, motors, circuit breakers, radiators, drying chambers and the like from overheating. It makes possible the quick determination of isothermals on airplane motor cylinders, indication of faulty insulation on heating tanks and the detection of burners which have "struck-back."

Thermocolors are made of salts of different metals (particularly copper, cobalt, nickel, chromium, molybdenum and uranium) in compounds which change color at certain temperatures through loss of water, ammonia, carbon dioxide, through change from orthosalts to pyrosalts. Table II is a list of thermocolors, all of which are organic or inorganic compounds with ammonia which contain colored ions. It will be noted that some pigments show multiple color changes. This suggests the goal of a thermocolor paint which can be

TABLE II<sup>6</sup>  
THERMOCOLORS

Thermocolor	Temperature	Color change on heating	
1. $(\text{NH}_4)_2\text{U}_2\text{O}_7$ .....	200°C.	Yellow	Gray
2. $(\text{NH}_4)_4\text{H}_6[\text{Ni}(\text{MoO}_4)_6] \cdot 5\text{H}_2\text{O}$ ...	180–210	White	Gray
3. $(\text{NH}_4)_3\text{H}_6[\text{Fe}(\text{MoO}_4)] \cdot 7\text{H}_2\text{O}$ ...	80	White	Yellow
4. $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .....	140–160	Yellow	Black
5. $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ .....	140	Purple red	Deep blue
	500	Deep blue	Bright green
6. $\text{NiNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .....	120	Bright green	Gray green
7. $\text{NH}_4\text{MnP}_2\text{O}_7$ .....	400	Violet	White
8. $[\text{Co}(\text{NH}_3)_4]\text{PO}_4$ .....	200	Yellow	Blue
9. $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3$ .....	210–220	Yellow	Violet
	250–270	Violet	Brown
	320–350	Brown	Black
10. $[\text{Co}(\text{NH}_3)_6]\text{HP}_2\text{O}_7$ .....	280	Yellow	Blue gray
	~400	Blue gray	Bright violet
11. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .....	190	Purple	Dark blue
12. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SiF}_6$ .....	200	Purple	Gray
13. $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6]$ .....	140	Green	Brown
14. $[\text{Ni pyraz}](\text{CNS})_2$ .....	135	Blue	Bright green
	210	Bright green	Yellow
	340	Yellow	Brown
15. $[\text{Cu pyraz}](\text{CNS})_2$ .....	135	Green	Yellow
	220	Yellow	Black
16. $[\text{Cr}(\text{NH}_3)_6]_4(\text{P}_2\text{O}_7)_3$ .....	140–150	Yellow	Violet
	220–230	Violet	Bright blue
	280	Bright blue	Brown
17. $[\text{Cr}(\text{NH}_3)_5\text{Cl}_2]\text{O}_4$ .....	260	Red	Dark brown
18. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SiF}_6$ .....	250	Red	Dark brown
19. $\text{NH}_4\text{UO}_3$ .....	150	White	Brownish
	170	Brownish	Black

sprayed on a surface to indicate at a glance its temperature, over a wide range of values.

For some application reversible color changes are suitable, but more often irreversible changes are desired for per-

<sup>6</sup> Penzig, *Chem. Fabrik*, 12, 277, 358 (1939); [DRP 665 462].

manent indications. It is difficult to find colors whose changes are stable at low temperatures. The thermocolors listed in Table II are irreversible. The color change is somewhat dependent on time as well as temperature: for rapid heating it occurs at higher temperature.

### Photothermometry

With the development of infra-red sensitive photographic plates it has become possible to photograph hot bodies by their own radiation and from the photographs to determine temperatures. The blackening of the photographic plate depends on the temperature of the source since each temperature is characterized by a definite radiation energy. The lower limit of usefulness for photothermometry is determined by plate sensitivity and intensity of radiation. It is approximately 250–270°C. for large aperture lenses and 15 hour exposures. There is no upper limit. There is a rapid increase in radiation energy with temperature. As the temperature increases from 275 to 400°C. the radiation energy (for  $\lambda = 0.85\mu$ ) increases from  $3.23 \times 10^{-6}$  to  $933 \times 10^{-6}$  cal. cm.<sup>-2</sup> The method of photothermometry is not good for absolute measurements. Uncertainties may be of the order of 60–120°C. It does, however, determine temperature ratios with good accuracy, and is particularly useful in obtaining quickly the isothermals of engine cylinders, furnaces, insulating jackets and the like.

The monochromatic radiation energies  $E_1$  and  $E_2$  corresponding to source temperatures  $T_1$  and  $T_2$  are related by

$$\log E_1 - \log E_2 = \frac{a}{\lambda} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad (3)$$

For small temperature differences the quantity in brackets may be replaced by  $b(T_1 - T_2)$ . In calibrating the photographic plate, temperature differences, proportional to logarithms of energy, are plotted as abscissas and plate darkening

as ordinates, giving curves similar to the familiar density—log intensity curves of ordinary photography.<sup>7</sup>

TABLE III<sup>8</sup>  
EXPOSURE TABLE FOR INFRA-RED PHOTOGRAPHY  
(Agfa 850 plate. Dark room. No filter. Distance: 6 feet.)

Temperature	Relative aperture				
	1.5	2.7	3.1	4.5	6.3
800°C. to 910°C.	$\frac{1}{40}$ sec.	$\frac{1}{25}$ sec.	$\frac{1}{10}$ sec.	$\frac{1}{6}$ sec.	$\frac{1}{2}$ sec.
700 780	$\frac{1}{25}$	$\frac{1}{6}$	$\frac{1}{2}$	1	3
600 680	$\frac{1}{2}$	2	4	10	30
550 625	1	6	10	30	1.5 min.
500 570	5	30	50	2.5 min.	7.5
450 520	30	3 min.	5 min.	15	45
400 470	25	17	30	1 hr. 30 min.	4 hr. 30 min.
{ Plate sensitized	35 sec.	3.5	6	18 min.	1 hr.
{ 350 420	30 min.	3 hr.	4 $\frac{1}{2}$ hr.	15 hr.	
{ Plate sensitized	8	50 min.	1 hr. 20 min.	4 hr. 10 min.	12 hr. 30 min.
{ 325 380	2 hr. 15 min.	15 hr.	24 hr.		
{ Plate sensitized	35 min.	4	6 hr. 15 min.	20	
{ 300 350	8 hr. 30 min.				
{ Plate sensitized	2 hr. 15 min.	15			
{ Plate sensitized and pre-					
exposed	35 min.	2 hr. 15 min.	4 hr. 30 min.	14 hr. 10 min.	
{ 275 325	27 hr.				
{ Plate sensitized	7 hr. 45 min.				
{ Plates sensitized and pre-					
exposed	2 hr. 15 min.	15	24		

For black filters (Agfa 85 & 87): multiply times by 2 for twilight, green or strongly-colored lamp light, for surfaces which are black, oxidized or colored. For smooth surfaces, white or painted bronze: multiply by 10.

For red filters (agfa 81 to 84): no change in exposures tabulated.

The standard used in calibrating the plate may be an electrically-heated nickel cylinder whose temperature is measured with a thermocouple. Rapid calibration from a single exposure is made by photographing the temperature parabola existing in an aluminum or silver rod heated at one end.

<sup>7</sup> See, for example, J. E. Mack and M. J. Martin, *The Photographic Process*, New York: McGraw-Hill, 1939. Chap. 6.

<sup>8</sup> P. Neubert, *Arch. Warmewirt.*, 19, 30 (1938) [Bibliography].

Commercial infra-red plates are available for photothermometry.<sup>9</sup> These are best stored in a refrigerator and used within a few months. They may be sensitized with ammonia immediately before use. Rodinal developer is used for steep gradation, or metol-hydroquinone or glycine for smaller  $\gamma$ .

Photothermometry in a darkened room requires no filters. If extraneous light is present it is kept from the plate by a red or "black" filter, such as a cobalt oxide glass which has been heated to blackness. Table III gives exposure data for photothermometry.

### Interferometer measurement of temperature

The "heat waves" often seen near a hot surface suggest a possible method of measuring temperature. Schmidt<sup>10</sup> demonstrated that photographs of the atmospheric streaks in a temperature field near a hot body were susceptible of quantitative measurement. Kennard<sup>11</sup> used a more sensitive interferometer method to investigate isothermal patterns, to calculate convective heat transfer and to investigate how closely film theory agreed with experiment.

The Mach interferometer used by Kennard is represented in Fig. 131, where  $H$  is the test body (plate or cylinder) of length  $L$ ,  $AA$  is the plane in which the fringes were brought to virtual focus, and  $F$  is a filter which transmits only the green mercury light.  $T$  is a shielded thermocouple.

The method of measuring temperature from fringe shift can be indicated with the aid of Fig. 132. Let  $A$  and  $B$  be two adjacent fringes formed by monochromatic light passing through the column of air adjacent to the heated surface  $H$ . The shift of one fringe at  $P$  relative to  $Q$  indicates that there is one less light wave in the path through  $P$  than there would

<sup>9</sup> *Agfa 700, 800 and 850 plates.* (The numbers indicate the wavelength of maximum sensitivity in millimicrons,  $= 10^{-7}$  cm.) *Eastman R, P, M, Q and Z plates.*

<sup>10</sup> E. Schmidt, *Forsch. Gebiete Ingenieurw.*, A3, 181 (1932).

<sup>11</sup> R. B. Kennard, *Bur. Standards J. Research*, 3, 787 (1932).

be if the temperature of  $P$  were the same as at  $Q$ . The temperature of the air is obtained from its density which is

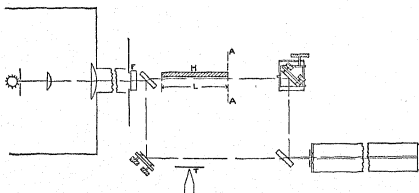


FIG. 131.—Interferometer for temperature measurement.

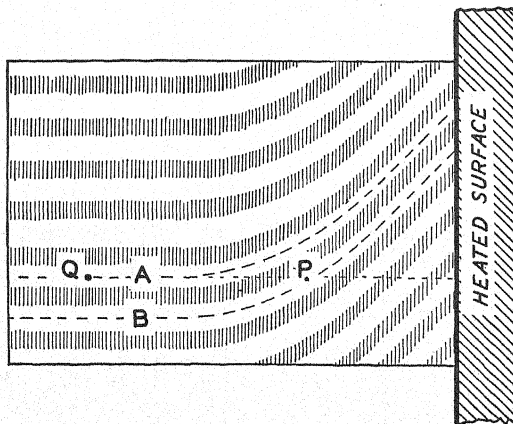


FIG. 132.—Method of measuring temperature from fringe shift.

related to the refractive index by the Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} = C\rho \quad (4)$$

where  $n$  is the index of refraction,  $\rho$  the density, and  $C$  is a constant. For an index of refraction of the order of 1.0003 this reduces approximately to

$$n - 1 = \frac{3}{2}C\rho. \quad (5)$$

If, under one set of conditions,  $N_1$  and  $n_1$  are the number of light waves over a given path, and the index of refraction, respectively, and  $N_2$  and  $n_2$  are the same quantities for a second set of conditions,

$$n_1 = \frac{N_1}{N_0} \quad \text{and} \quad n_2 = \frac{N_2}{N_0} \quad (6)$$

where  $N_0$  is the number of light waves in the same path in a vacuum.

If  $L$  is the length of path under consideration, which is the length of the heated surface  $L_0$  plus a small end correction  $\Delta L$ , and if  $\lambda_0$  is the wavelength in vacuum of the light used,

$$N_0 = \frac{L}{\lambda_0} \quad (7)$$

From Eq. 5 the change of index of refraction for a given change in density is

$$n_1 - n_2 = \frac{3}{2}C(\rho_1 - \rho_2) \quad (8)$$

Inserting the values given in Eq. 6 and 7 and rearranging yields

$$N_1 - N_2 = \frac{3}{2}C\rho_1 \frac{L}{\lambda_0} \left(1 - \frac{\rho_2}{\rho_1}\right) = (n_1 - 1) \frac{L}{\lambda_0} \left(1 - \frac{\rho_2}{\rho_1}\right) \quad (9)$$

If the change in density is caused by a change in temperature only

$$\frac{\rho_2}{\rho_1} = \frac{T_1}{T_2} \quad (10)$$

whence

$$N_1 = N_2 = (n_1 - 1) \frac{L}{\lambda_0} \frac{T_2 - T_1}{T_2} \quad (11)$$



Since in the interferometer the change in number of light waves in a given path is equal to the fringe displacement, Eq. 11 gives the fringe displacement as measured in fringe widths that takes place when the temperature is changed from  $T_1$  to  $T_2$ . Letting  $T_1$  and  $n_1$  be the temperature and index of refraction of room air, Eq. 11 may be solved

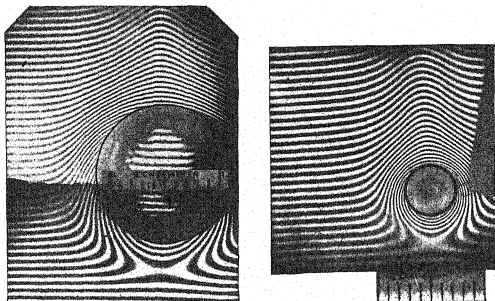


FIG. 133.—Fringes about horizontal heated cylinders.

explicitly for the temperature rise above the air of the room giving

$$T_2 - T_1 = T_1 \frac{\Delta N}{(n_1 - 1) \frac{L}{\lambda_0} - \Delta N} \quad (12)$$

The quantity  $(n_1 - 1)$  is given in the International Critical Tables for standard conditions and may be calculated for any conditions by using the gas laws, making proper correction for humidity.

Figure 133 is a photograph of the interference fringe pattern observed in the air near two horizontal heated cylinders of diameters 1.27 cm. and 5 mm. respectively. Figure 134 shows the isothermals for free convection calculated from the fringe pattern. In practical problems heating surfaces are often

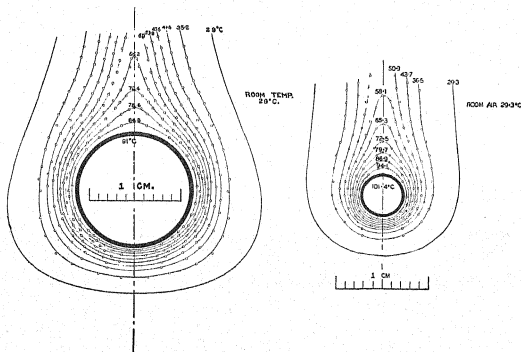


FIG. 134.—Isotherms about horizontal heated cylinders.

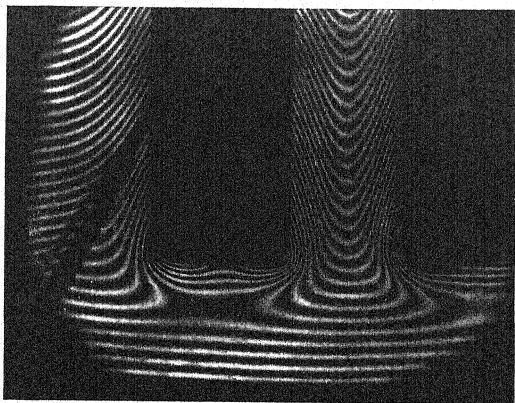


FIG. 135.—Fringes about parallel, vertical heated plates.

in the form of parallel plates. Figure 135 shows the interference fringes about the lower portion of two vertical parallel plates, size 11 cm. wide and 21.4 cm. high, separated by 0.67 cm. Such a pattern can be used to measure heat flux.

### Summary

Experience in measuring gas temperatures emphasizes the necessity of securing thermal equilibrium between pyrometer and gas. Accuracy is enhanced by providing adequate convection, by preventing or compensating for radiation losses and by using a pyrometer only under the conditions for which it has been calibrated. The spectral line reversal method uses Kirchhoff's law to measure the temperature of luminous and non-luminous flames, being applicable in particular to the study of internal combustion engine temperatures. Pyrometric cones indicate heat treatment, in which factors other than temperature must be considered. Thermocolors provide visual indication of surface temperatures, chiefly valuable in warning of overheating. Photothermometry, based on laws of radiation and photography, permits rapid determination of temperature and isothermals over extended surfaces. Another photographic method uses an interferometer to measure temperature in terms of refractive index, being useful in designing radiating surfaces for optimum heat transfer.

## CHAPTER XIV

# Extreme Temperatures

## Low Temperatures

### Introduction

The existence of a theoretical lower limit to temperature is a challenge to produce successively lower temperatures in the laboratory. Progress toward the absolute zero is not merely directed to the creation of new records but to actual study of effects associated with energy changes of such magnitude that only in this region can they be observed. Herein lies the importance of being able to attain in the laboratory a temperature of  $0.0034^{\circ}\text{K.}$ , lower even than the temperature (about  $2^{\circ}\text{K.}$ ) of interstellar space.

Processes used to produce cooling are: (1) solution of salts, acids or gases in water or ice; (2) evaporation of a liquid; (3) adiabatic expansion of a gas with performance of external work; (4) controlled expansion of a gas utilizing the Joule-Thomson effect; (5) adsorption; and (6) adiabatic demagnetization.

Figure 136 represents the behavior of a freezing solution. When salt comes in contact with ice in an excessive quantity it forms a solution which in turn dissolves more ice. If the mixture is thermally insulated the heat required to transform the ice comes from the internal energy of the mixture itself, lowering its temperature. This action continues until point *E*, the eutectic, is reached.

If a liquid is thermally insulated and allowed to evaporate, the required latent heat of evaporation is supplied by the liquid itself and its temperature is reduced. If the vapor is carried away, more liquid evaporates and its temperature

further decreases. By continually pumping the vapor from liquid helium placed in a Dewar flask a temperature as low as  $0.7^{\circ}\text{K.}$  is reached.

### Liquefaction of gases; thermodynamics

Andrews showed in 1863 that it is possible to liquefy a gas only if the pressure exceeds a critical value  $p_c$  and the temperature is below a critical value  $T_c$ . The critical constants  $p_c$  and  $T_c$  are properties of the gas. Their numerical

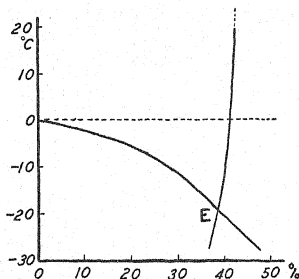


FIG. 136.—Equilibrium diagram for ice and ammonium sulphate.

values may be calculated if the equation of state is known. Assuming that Van der Waal's equation is applicable,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

the critical constants may be obtained by equating  $\delta p / \delta v$  and  $\delta^2 p / \delta v^2$  to zero,

$$T_c = \frac{8a}{27bR} \quad p_c = \frac{1a}{27b^2}$$

If gas molecules, instead of being enclosed in a vessel with fixed walls, are reflected from, say, a receding piston, their velocities are lowered and the temperature of the gas falls.

By this method temperature is reduced by the conversion of heat into external work. A second method of cooling a gas is to allow it to expand, i.e., allow the molecules to recede from each other. If there is appreciable mutual attraction it will tend to reduce their speed as they move apart, lowering the temperature. This is the Joule-Thomson effect.

*Adiabatic expansion of a gas* from  $p_1$  to  $p_0$  can produce external work  $M \int_{v_1}^{v_0} p dv$ , reducing the energy of the gas by an equal amount. If  $u$  is the energy per unit mass

$$p dv = -du = -\left(\frac{\delta u}{\delta T}\right)_v dT - \left(\frac{\delta u}{\delta v}\right)_T dv \quad (1)$$

but  $(\delta u / \delta T)_v = C_v$  the specific heat at constant volume, and the second law provides

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\delta p}{\delta T}\right)_v - p$$

hence

$$dT = -\frac{T(\partial p / \partial T)_v}{C_v} dv$$

For a perfect gas this becomes  $dT = -T \frac{C_p - C_v}{C_v} \frac{dv}{v} = T(\gamma - 1)dv$  or

$$\frac{T_0}{T_i} = \left(\frac{v_i}{v_0}\right)^{\gamma-1} \quad (2)$$

This represents the method used by Cailletet to liquefy air, hydrogen, etc., and is the basis of the Claude and Heylandt methods of liquefying air.

*The Joule-Thomson effect* produces a change in temperature in a current of gas when it expands adiabatically through a porous plug against constant external pressure. The gas loses energy during its passage through the plug (Fig. 137). The total heat  $i = u + pv$  remains constant. The change in entropy is given by  $dS = (du + p dv) / T$ . Also

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

When  $du$  is eliminated,

$$\left(\frac{\partial T}{\partial p}\right)_i = \left\{ T \left(\frac{\partial v}{\partial T}\right)_p - v \right\} \frac{1}{C_p} = \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{v}{T}\right)_p \quad (3)$$

Eq. 3 is for the Differential Joule-Thomson effect. The integral Joule-Thomson effect is given by

$$\Delta T_i = \int_{p_1}^{p_2} \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{v}{T}\right)_p dp_i$$

For a given pressure there exists a so-called inversion temperature at which the Joule-Thomson effect changes

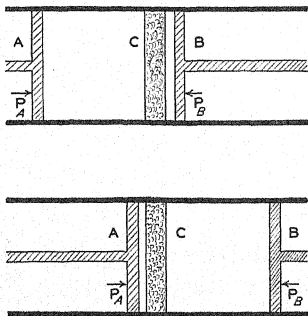


FIG. 137.—The porous plug experiment.

sign. Thus if a gas is allowed to expand under suitable conditions it can perform external work and produce the desired cooling.

### Liquefaction of gases: experimental technic

Carl von Linde first liquefied air on a commercial scale (1896) using heat exchangers and the Joule-Thomson effect. Such a process is represented schematically by Fig. 138. Air enters *I* at a pressure of 1 atm. Dust and carbon dioxide

are removed at  $W$ . The air is compressed to 200 atm. at  $C$ , from where it passes through drying tube  $D$  into chamber  $A$  surrounded by ammonia freezing mixture where it is cooled to  $-50^{\circ}\text{C}$ . It then enters the heat exchanger  $E$  and passes the valve  $V$  where the pressure is reduced to 20–50 atm. A large part of the expanded air returns through  $E$  to the compressor, but a small part is liquefied and passes through tap  $T_1$  into  $R$ . Liquid air from  $R$  can be removed by tap

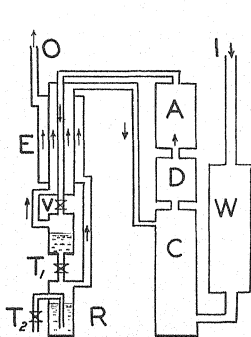


Fig. 138.—Linde air liquefier.

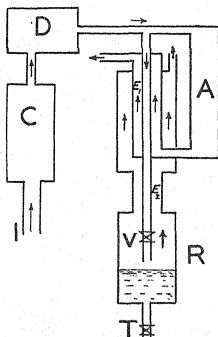


Fig. 139.—Claude and Heylandt air liquefier.

$T_2$ , while air evaporating in  $R$  passes through  $E$  and into the atmosphere at  $O$ . In operation only sufficient air to replace the liquid removed enters at  $I$ .

In the type of plant used by Claude and Heylandt (Fig. 139) purified air enters  $C$  where it is compressed to 200 atm. After passing through dryer  $D$ , the current branches. Part goes into engine  $A$  where it performs work, expands to 1 atm. and is cooled, and then passes through heat exchanger  $E_1$ . The other part goes through  $E_1$  where it is cooled and then is expanded to 1 atm. at valve  $V$ . Some of the air is liquefied upon expansion and remains in  $R$ . The rest passes through



exchanger  $E_2$  and escapes into the atmosphere. About 25% of the air compressed is liquefied.

For the liquefaction of hydrogen and helium, the adiabatic expansion method, used by Olszewski to liquefy hydrogen (1895) and by Simon to liquefy helium (1933), is convenient only for obtaining small quantities. High pressures and pre-cooling with evaporating nitrogen or hydrogen are necessary.

The method of allowing the gas to expand while doing internal work (Joule-Thomson effect), used by Dewar to liquefy hydrogen (1898) was the only method used for large-scale production of liquid hydrogen and helium until 1934. The method was improved by Onnes, Lilienfeld and Meissner who introduced safety devices to minimize the danger of explosion always present when working with large quantities of hydrogen. Since helium approximates an ideal gas its Joule-Thomson effect is small, and the liquefaction process has a low efficiency, only about 1% that of the adiabatic method.

The great advantage of liquefying gases by making them do work on a mechanical system has long been recognized. Claude used an expansion engine of the reciprocating piston type successfully to liquefy air, but due to the difficulty of lubrication the method cannot readily be applied to hydrogen or helium.

Kapitza constructed an expansion engine<sup>1</sup> in which the piston required no lubrication. The piston is loosely-fitted in the cylinder with a definite clearance (0.05 mm.) and is provided with tiny circular grooves on its circumference to equalize the gas pressure in the gap. Turbulent flow of gas through the gap between cylinder and piston furnishes lubrication. The loss through leakage is only a few per cent, since the piston is arranged to move very rapidly on the expanding stroke. The cooled gas obtained by this adiabatic expansion is then allowed to cool a portion of the incoming

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<sup>1</sup> P. Kapitza, *Proc. Roy. Soc. (London)*, 147, 189 (1934); *Nature*, 133, 208 (1934).

gas as in Claude's apparatus. The compressed gas becomes cooled and during the final stage it is allowed to undergo Joule-Thomson expansion, as in Heylandt's method, and becomes liquefied.

The expansion engine employed by Kapitza, with its hydraulic device for securing quick expansion and slow compression, is shown in Fig. 140. The expansion machine *E* is connected by rod 1 to the hydraulic press *H*. The high pressure gas enters the cylinder past the ball valve 2 and expands adiabatically, pushing forward the pistons 3 and 4. The gas transforms its internal energy into kinetic energy of the water which is expelled from orifice 5. The backward stroke is caused by water gradually filling *H*. The valves are actuated by electromagnets. Since rod 1 has the same diameter as piston 3, the expansion

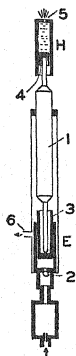


FIG. 140.  
Expansion engine.

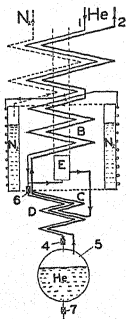


FIG. 141.—  
Cooling circuit for  
liquefying helium.

stroke can be very rapid and yet preserve a smooth flow of cooled hydrogen or helium from 6 to the heat exchanger.

The arrangement of the liquid circulation is indicated in Fig. 141, where tubes are represented by lines. Compressed helium enters tube 1, passes through the heat exchanger *A* and then is cooled to 65°K. by passing around a ring-shaped vessel *N* containing liquid nitrogen boiling at reduced pressure. It passes through heat exchanger *B* to the expansion engine *E* where it cools by adiabatic expansion. It then goes through the heat exchanger *CBA* and 2 to the compressor. After a few cycles the temperature falls considerably and the throttle valves 6 and 4 are opened. The gas experiences a Joule-Thomson expansion at 6, passes through the heat exchanger *CD* and suffers another Joule-Thomson

expansion at 4 and liquefies in 5. Helium gas from 5 passes through heat exchanger *DCB* to 2.

The starting time of the liquefier is  $1\frac{1}{4}$  hr., and the output is 2 liter/hr. using  $1\frac{1}{2}$  liters of liquid nitrogen to produce 1 liter of liquid helium.

Kapitza<sup>2</sup> has recently investigated the thermodynamic conditions under which liquefaction at low pressure (5–6 atm.)

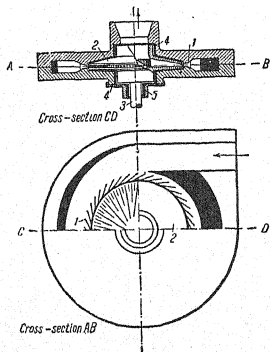


FIG. 142.—Construction of turbine.

is possible. This can be accomplished, for air, by the use of an expansion turbine, whose efficiency is improved by making use of centrifugal forces. On these principles he has constructed an air liquefier whose efficiency is 83%. It has a short starting period (18–20 min.) and an output of 30 kg. of liquid air per hour.

The turbine is illustrated in Fig. 142 which shows the shape of the nozzles 1 and of the rotor blades 2. The rotor is made of monel, has

a diameter of 8 cm. and is normally run at 41,000 r.p.m. To prevent air flowing past the blades, two labyrinth glands 4, with a clearance of 0.15 mm., are provided. Figure 143 shows the general arrangement of the installation. Air is admitted through the filter 1 to the compressor 2 where it is compressed to 6–7 atm. The flow of compressed air passes through the water cooler 3, the oil purifier 4, and enters the valve system 5 of the regenerators 6. The slide valve is actuated by electromagnets, reversing its stroke every 25–27 sec. Passing valves 7, the flow of compressed air divides. The main bulk of air, after passing a filter and a

<sup>2</sup> P. Kapitza, *J. Physics (USSR)*, 1, 7 (1939).

temperature equalizer 8, enters expansion turbine 9, where it expands and then returns through condenser 10 into the other exchanger and escapes into the atmosphere. Work produced on the turbine is absorbed by a water brake at the rate of 4 kw. The remaining flow of compressed air is delivered through the check valve 11 to the condenser 10 where it liquifies. The liquid air is drawn off into container 13, from which it may be removed through tap 14.

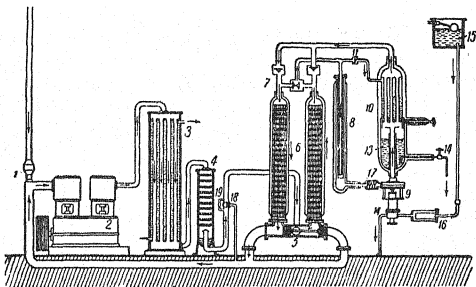


FIG. 143.—Liquid air plant using turbine expansion engine.

### Absorption and desorption

In Simon's process helium comes in contact with an absorbent substance, such as charcoal or chabazite, at the temperature of liquid hydrogen. The heat of absorption of helium is removed by a liquid hydrogen bath. The system is then thermally isolated and the helium pumped off the absorbing surface. Desorption cools the helium below its critical temperature and expansion results in its liquefaction.

### Adiabatic demagnetization

The lowest temperature reached by decreasing the pressure over liquid helium is about  $0.7^{\circ}\text{K}$ . A totally different method, originally suggested by Debye and Giaque,<sup>3</sup> has

<sup>3</sup> P. Debye, *Ann. Physik*, 81, 1154 (1926).

W. F. Giaque, *J. Am. Chem. Soc.*, 49, 1984 (1927).

resulted in the attainment of a new temperature region. The entropy of a substance is a measure of its state of disorder. A group of molecules at rest in an accurate space-lattice would be in a state of complete order, that is, its entropy would be zero. If the molecules acquire motion the entropy increases. Paramagnetic salts contain atoms which behave like small magnets. If an external field is applied the axes of the magnets will tend to be aligned. The entropy due to their positional disorder will therefore decrease. Hence, if the substance is thermally insulated the entropy of their thermal motions must increase, that is heat will be developed. If this heat is removed, say, by placing the substance in contact with liquid helium, and the substance is then again thermally insulated, it is clear that one can cool the substance by reversing the process. For when the external magnetic field is removed, the axes of the atomic magnets will tend, under the influence of thermal agitation, to resume their disordered condition. The positional entropy will increase at the expense of the entropy of agitation and the temperature will decrease.

One might assume that to secure good results with the adiabatic demagnetization method: (1) The elementary magnets should not exert a directing influence on each other, *i.e.*, the substance should not be ferromagnetic. (2) The elementary magnets should have moments as large as possible, subject to the previous restriction. (3) The effect should be greatest at low temperature since there the entropy associated with magnetization is an appreciable part of the total entropy, and also the order is greatly increased.

During the adiabatic demagnetization the entropy is constant and the pressure is constant (a vacuum). Hence

$$dS = \left( \frac{\partial S}{\partial H} \right)_{p,T} dH + \left( \frac{\partial S}{\partial T} \right)_{p,H} dT = 0$$

$$dT = \frac{(\partial S / \partial H)_{p,T}}{(\partial S / \partial T)_{p,H}} dH$$

Since the process is reversible  $dS = dQ/T$ . The quantity of heat  $dQ$  added to the substance is  $dU + pdV + HV\chi dH$ , where  $U$  is the internal energy,  $V$  the mol volume and  $\chi$  the susceptibility per cm.<sup>3</sup> Writing  $J = U + pV$ ,

$$dS = \frac{dQ}{T} = \frac{dJ - Vdp + HV\chi dH}{T}$$

hence

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_{p,H} &= \frac{1}{T} \left(\frac{\partial J}{\partial T}\right)_{p,H} = \frac{C_{p,H}}{T} \\ \left(\frac{\partial S}{\partial H}\right)_{p,T} &= \frac{1}{T} \left\{ \left(\frac{\partial J}{\partial H}\right)_{p,T} + HV\chi \right\} \end{aligned}$$

This means that  $C_p$  is also a function of  $H$ . Since  $dS$  is a perfect differential,

$$\frac{\partial^2 S}{\partial T \partial H} = \frac{\partial^2 S}{\partial H \partial T}$$

giving

$$\left(\frac{\partial J}{\partial H}\right)_{p,T} + HV\chi = TH \left[ \frac{\partial}{\partial T} (V\chi) \right]_{p,H}$$

and

$$\left(\frac{\partial S}{\partial H}\right)_{p,T} = H \left[ \frac{\partial}{\partial T} (V\chi) \right]_{p,H}$$

which leads to

$$dT = - \frac{TH \left[ \frac{\partial}{\partial T} (V\chi) \right]_{p,H}}{C_{p,H}} dH \quad (4)$$

To make  $dT$  large,  $\frac{\partial}{\partial T} (V\chi)$  must be large and  $C_{p,H}$  small.

Substances which obey the Curie-Langevin law  $\chi = c/T$  even at lowest temperatures are best suited for the magneto-calorific effect. In them the magnetic atoms are widely separated so mutual interactions are small. The same advantage may be secured by using compounds in which the magnetic atoms are diluted by the presence of other atoms.

Results obtained by Kürti and Simon<sup>4</sup> using apparatus similar to Fig. 144 are listed in Table I and others obtained

<sup>4</sup> N. Kürti and F. Simon, *Proc. Roy. Soc.*, **149**, 152 (1935).

by de Haas<sup>5</sup> in Table II.  $T_i$  and  $H_i$  represent initial values of temperature and magnetic field strength,  $T_f$  and  $H_f$ , respectively, their final values. The possibility of attainment of still lower temperatures seems to lie in the use of nuclear spins of metals, where the magnetic energy can be transferred between nuclear spin and conduction electrons in a time short enough to allow further application of the magnetic cooling method.

TABLE I

Substance	$T_i$ °K.	$H$ oersted	$T_f$ °K.
Ironammonium alum } FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O } .....	{ 1.23 1.23 2.23	14,100 2,900 10,300	0.038 0.187 0.099
MnSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O .....	1.23	8,000	0.09
½Gd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O .....	1.15	5,400	0.35
KCr(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O .....	1.16	24,600	0.031
1[MnSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O] + } 20[MgSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O] } .....	?	?	0.05 to .08

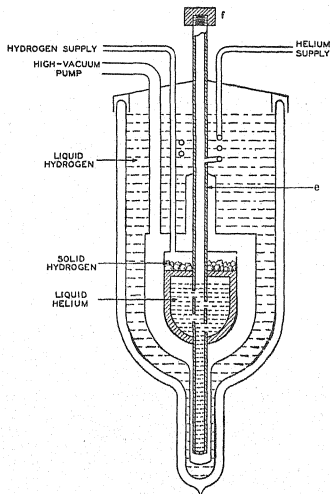
TABLE II

Substance	$H_i$ oersted	$H_f$ oersted	$T_i$ °K.	$T_f$ °K.
CeF <sub>3</sub> .....	{ 27,600 27,600 27,600	4,500 2,200 850	1.314 1.314 1.314	0.27 .19 .13
Ds(C <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O .....	19,500	200	1.314	.12
Ce(C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O .....	27,600	850	1.314	.09
K <sub>2</sub> SO <sub>4</sub> Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O .....	19,500	350	1.314	.05
CS <sub>2</sub> SO <sub>4</sub> Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O .....	25,075	1.0	1.314	.0055
1[K <sub>2</sub> SO <sub>4</sub> Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O] + } 14.4[K <sub>2</sub> SO <sub>4</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O] } .....	24,075	1.0	1.92	.0044

Low temperatures are generally measured with helium thermometers. They are reduced to the thermodynamic

<sup>5</sup> W. J. de Haas, *Natuurw.*, 23, 180 (1935).

scale by using the principle that when a gas is used at successively lower pressures the corresponding gas scale of temperature approaches the thermodynamic scale. In the range from 0.7 to 5.0°K. the vapor pressure of helium gives the temperature, using various empirical formulas. At still lower



CRYOSTAT FOR LIQUID HELIUM

FIG. 144.—Cryostat for cooling by adiabatic demagnetization. [K. K. Darrow, *Rev. Sci. Instruments*, 12, 1, (1941).]

temperatures the vapor pressure of helium decreases exponentially, as shown in Table III,<sup>6</sup> and an alternative method of measuring temperature is necessary.

The paramagnetic substances used in attaining the lowest temperatures may be made to indicate their own temperatures

<sup>6</sup> W. H. Keesom, *Comm. Kamerlingh Onnes Lab. Univ. Leiden*, 219a (1932).



in terms of magnetic susceptibility:  $\chi \propto 1/T$ . In Simon's method, two coils are placed around the specimen, an alternating current produced in one and the other connected to a galvanometer. The electric circuit is so compensated that the galvanometer deflection varies inversely as the temperature. De Haas uses a sensitive balance to measure the force on the specimen when placed in a non-homogeneous field.

From  $F = MV\chi H \frac{\partial H}{\partial x}$ , (where  $M$  is the mol number and  $H$  and  $\partial H/\partial x$  are constant) and from Curie's law, it is evident that the force is inversely proportional to the absolute temperature.

TABLE III  
VAPOR PRESSURE OF LIQUID HELIUM

Deg. K.	Mm. Hg
4.219	760
1.714	10
1.237	1.0
1.00	$1.5 \times 10^{-1}$
0.50	$2.5 \times 10^{-5}$
0.30	$7 \times 10^{-10}$
0.10	$3 \times 10^{-31}$
0.03	$6 \times 10^{-103}$

The number of laboratories equipped to produce liquid hydrogen, liquid helium or both (now 15 in the United States) is increasing, and with it the need for a procedure simpler than the direct use of a gas thermometer for measuring low temperatures. The international temperature scale is not defined below 83°K. (−190°C.). There is no satisfactory simple formula relating the resistance of platinum and the temperature in this region. However, tables have been published<sup>7</sup> extending the useful range of the platinum resistance thermometer from 83°K. to 14°K.

The temperature coefficient of resistance of most metals approaches zero in the liquid helium region. Many experi-

<sup>7</sup> H. J. Hoge and F. G. Brickwedde, *J. Research Nat. Bur. Standards*, **22**, 351 (1939).

ments in search of substances suitable for resistance measurements at lower temperature have suggested the use of an alloy of 5% lead in silver for the range from 7° to 3°K.,<sup>8</sup> and unannealed phosphor-bronze for the range from 4.2° to 1°K.<sup>9</sup>

## High Temperatures

### Introduction

There is no generally accepted upper limit to temperature. Various limiting values of the order of  $10^{12}$  °K. have been suggested<sup>10</sup> on theoretical grounds, based on assumptions of questionable validity. The attainment of high temperatures for useful purposes is limited by the materials available for construction and the difficulty of securing a controlled, uniform temperature. The temperature in industrial metallurgical processes seldom exceeds 1700°C., while 3000°C. is the highest temperature commonly used in the laboratory.

### Refractory materials

There is a progressive failure of all materials of construction at high temperature by (1) decomposition or alteration, (2) oxidation, (3) fracture of flow, or (4) fusion. Asbestos disintegrates by loss of water with the formation of powdery silicate of magnesia. Vitreous silica crystallizes at 1200°C. and higher to become powdery white cristobalite. Oxidation of metals is avoided by use of a protecting atmosphere of hydrogen, nitrogen or helium, or by the use of iron-nickel-chromium alloys and such high temperature metals as tungsten and molybdenum. Silicon carbide is the only common refractory material which fails by oxidation rather than by fusion. Fracture is important in large industrial apparatus,

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<sup>8</sup> J. D. Babbit and K. Mendelssohn, *Phil. Mag.* (7), 20, 1025 (1934).

<sup>9</sup> W. H. Keesom and J. N. Van Den Ende, *Comm. Kamerlingh Onnes Lab. Univ. Leiden*, 203c (1929).

<sup>10</sup> G. I. Pokrovskii, *Z. Physik*, 51, 730 (1928).

B. Ptáček, *Chem. Obzor.*, 14, 129 (1939).

while for laboratory apparatus slow flow or shrinkage is usually more bothersome. This is due to the objectionable practice of adding plastic clay to some refractory materials. At the eutectic temperature ( $1545^{\circ}\text{C}$ . for the eutectic between mullite and cristobalite) a small amount of liquid is produced with consequent flow or shrinkage.

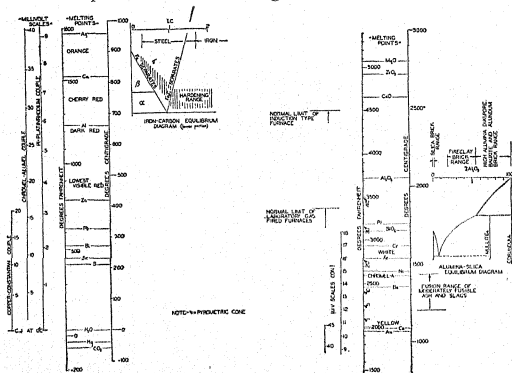


FIG. 145.—Temperature comparison chart. [T. C. Patton, *J. Chem. Education*, 9, 1110 (1932).]

In furnaces where heat is transferred to the charge from the exterior, the refractory walls must be subject to temperatures higher than needed for the sample.

Chemical reactions between the refractory container and the sample often require special precautions, especially in the case of tungsten.

Some refractory materials of commercial importance are listed in Table IV. Figure 145 is a comparison chart showing the location of the industrially-important iron-carbon and alumina-silica phase diagrams on a scale indicating temperatures and methods of temperature measurement.

TABLE IV  
MELTING POINT OF SOME MINERALS AND CERAMIC PRODUCTS

Material	Melting point (°C.)
Alumina brick.....	1750-2050
Bauxite brick.....	1730-1850
Carbon brick.....	2000
Chrome brick.....	1950-2200
Fireclay brick.....	1580-1880
Magnesite brick.....	2200
Mullite.....	1827
Porcelain, technical.....	1670-1920
Silica brick.....	1700-1750
Spinel.....	2135
Zircon brick.....	2200-2700

### Combustion furnaces

Temperatures attainable with various common flames, for combustion in either air or oxygen are listed in Table V. A burner for the combustion of oil in oxygen provides a

TABLE V  
TEMPERATURES FURNISHED BY VARIOUS FLAMES<sup>11</sup>

Gas	Combustion in air			Combustion in oxygen $t^{\circ}\text{C.}$
	Dissocia- tion of		$t^{\circ}\text{C.}$	
	H <sub>2</sub> O	C <sub>2</sub> O		
City gas + 6.5O <sub>2</sub> .....	0.02	0.12	1840	2800
City gas + 6.5O <sub>2</sub> with pre-heating of air to 1000°C.....	.07	.28	2200	
H <sub>2</sub> + $\frac{1}{2}$ O <sub>2</sub> .....	.03	....	2000	2700
CO + $\frac{1}{2}$ O <sub>2</sub> .....	....	.15	2025	2720
CH <sub>4</sub> + 2O <sub>2</sub> .....	.01	.10	1850	2850
C <sub>4</sub> H <sub>10</sub> + 6.5O <sub>2</sub> .....	....	....	1900	2900
C <sub>2</sub> H <sub>2</sub> + O <sub>2</sub> .....	.04	.19	2050	3100

<sup>11</sup> G. Ribaud, *Chaleur et ind.*, 35, 3 (1936).

temperature of  $2600^{\circ}\text{C}$ . The Langmuir atomic-hydrogen flame provides a temperature of  $3800^{\circ}\text{C}$ . It is strongly reducing, an advantage when melting tungsten or molybdenum. Molecular hydrogen is circulated around the tungsten electrode of an electric arc where it is dissociated. Recombination occurs in the flame with the evolution of heat. Combustion furnaces are designed to direct the flame on the sample when possible to minimize heat losses. Combustion furnaces generally do not have the ease of control of electric furnaces.

### Electric resistance furnaces

(a) *Carbon granule* furnaces utilize the heating effect of a current conducted between two electrodes through pulverized carbon placed around the specimen. Above  $1750^{\circ}\text{C}$ . the carbon reacts appreciably with the protecting tube. Uniformity of temperature is poor, since the current tends to follow the path of least resistance which is the region of highest temperature. In similar furnaces the substance to be heated is in powdered or liquid form and is itself the conductor of the heating current.

(b) *Wire wound* furnaces commonly have nichrome resistors for use up to  $1100^{\circ}\text{C}$ . or platinum for temperatures up to  $1400^{\circ}\text{C}$ . Heat transfer is facilitated by the use of large (1–3 mm. diameter) wire wound on the inside of a magnesia cylinder. Reaction occurs between the heating wire and its refractory support (above  $2000^{\circ}\text{C}$ . for tungsten or molybdenum). Using self-supporting spirals of molybdenum or tungsten one can attain temperatures of  $2300^{\circ}$  and  $2800^{\circ}\text{C}$ . respectively. Such a furnace is easily constructed and has a long life if the heater is in a reducing or neutral atmosphere. If an oxidizing atmosphere is needed for the sample the heating coil is wound on the outer surface of a refractory shell which is a good conductor, such as alundum. The furnace cannot be used above  $2000^{\circ}\text{C}$ . without the refractory tube becoming sufficiently permeable to gas to damage the heater.

(c) *Tubular furnaces* are efficient for heating small volumes. The conducting tube may be made of platinum, iridium, molybdenum or tungsten. This type is sturdy, but requires large current owing to its low resistance. Tubes of the Nernst type ( $\text{Zr}_2\text{O}_3$  85%,  $\text{Ti}_2\text{O}_3$  15%) have higher resistivity and are convenient for use at  $2300^\circ\text{C}$ .

There are various modified designs of tubular furnaces. One consists of rods laid parallel to the axis of the tube and

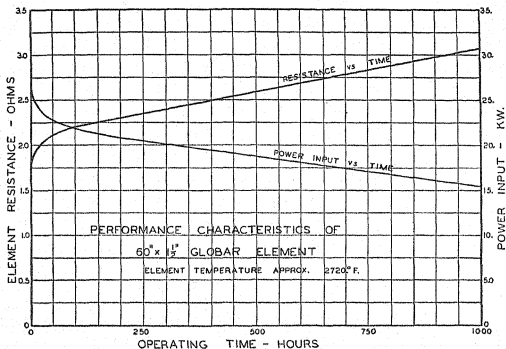
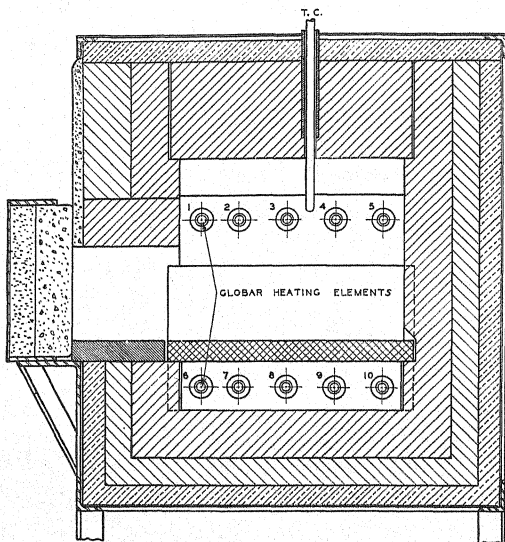


FIG. 146.—Performance characteristics of SiC heating elements. (The Carborundum Co., Globar Division.)

welded at their ends. Another is a graphite tube in which a helix has been cut to increase its resistance. The latter type attains  $3000^\circ\text{C}$ . in air, and can be used equally well in a vacuum where its useful temperature is limited by the evaporation of carbon to  $2400$ – $2800^\circ\text{C}$ .

(d) *Rod furnaces* use resistance rods of recrystallized silicon carbide which radiate directly into the volume to be heated. The elements have a negative temperature coefficient of resistivity up to about  $450^\circ\text{C}$ ., and a positive coefficient at higher temperature. Other performance characteristics

are illustrated by Fig. 146. It shows, for example, that since the resistance of the elements increases with time a



LEGEND :






 LIGHTWEIGHT REFRACTORY	 BLOCK INSULATION
 INSULATING BRICK	 FIRECLAY
 SILICON CARBIDE HEARTH	

Fig. 147.—Laboratory furnace with SiC heating elements.

furnace requiring 15 kw. to operate it must have elements having an initial power capacity of 27.5 kw. to obtain about 1000 hr. of service from them.

Such elements are used for furnace temperatures up to  $1500^{\circ}\text{C}$ . Since the heat is radiated from a small surface care must be used in designing the furnace to secure uniformity of temperature. Figure 147 shows the construction of a furnace for general laboratory use.

(e) *Arc furnaces* are most convenient for concentrating a large amount of heat in a small volume, permitting heating operations of short duration, an advantage for volatile substances. Temperatures up to  $3000^{\circ}\text{C}$ . may easily be maintained in an industrial furnace by the use of one or more arcs. The temperature of the arc itself varies from  $3400^{\circ}$  to  $4000^{\circ}\text{C}$ ., depending on current density, atmospheric pressure and the kind of electrode. The furnace atmosphere may be varied from oxidizing to reducing. Industrial arc furnaces are used in preparation of calcium carbide and steel, while in the laboratory they are used for fusing oxides of manganese, zirconium and thorium. Arc furnaces are not susceptible of precise control.

### **Furnaces without an auxilliary heating substance**

(a) *The high frequency induction furnace* consists of a solenoid producing an alternating magnetic field which can develop, by induction, a current in a conducting substance of any shape placed inside of it. The uniformity of temperature is best when the sample is a liquid metal, since it is then stirred electromagnetically. Uniformity is poorest when the sample is a solid of low thermal conductivity. Electrical non-conductors (refractory oxides) are surrounded with a conducting cylinder of tungsten or graphite and heated indirectly. Induction furnace temperatures are not limited by the characteristics of refractory materials. With an induction furnace conditions of high purity are attainable.

The alternating field needed for an induction furnace is produced by (1) a mercury arc with a condenser in parallel, (2) a rotary converter, (3) electron tubes. Figure 148 illustrates schematically an induction furnace. The secondary



of transformer  $T_2$  provides a high voltage which is interrupted at high frequency by the rotating spark gap  $E$ , producing a high-frequency alternating magnetic field in coil  $F$ . The furnace coil is water-cooled. Smooth control of heating is obtained through an induction regulator  $L$  and the various taps on transformer  $T_1$ .

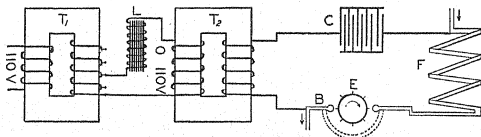


FIG. 148.—H.F. induction furnace.

(b) *Cathode ray furnaces* employ electron bombardment of the sample to produce heating. Since they operate only in a vacuum they are essentially laboratory apparatus.

(c) *Concentrated radiation furnaces* use mirrors to focus radiation on the specimen. By this method (Fig. 149) a

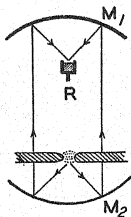


FIG. 149.—Carbon arc furnace with parabolic mirror.

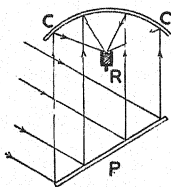


FIG. 150.—Sun furnace.

carbon arc may be used without contaminating the sample. In the furnace developed by Straubel, solar radiation (about  $1 \text{ kw. m.}^{-2}$  at the earth's surface) is concentrated by a heliostat and mirrors about 3 m. in diameter. A small tungsten cylinder placed at  $R$ , Fig. 150 is brought to  $3000^\circ$  in  $\frac{1}{2}$  min.

Since the maximum energy of the sun's spectrum lies just below  $1\mu$  it can be transmitted through walls of vitreous silica into an evacuated chamber without heating the walls. Rapid heating, conditions of purity, and, for some experiments, the absence of electric and magnetic fields are the advantages of the sun furnace. Its obvious disadvantages are cumbersome dimensions and an unreliable source of heat.

Very high temperatures are produced by electrically "exploding" a wire, by the discharge from a condenser. The extreme temperature is produced only momentarily. So far the temperature of the exploding wire, originally thought to be as high as  $20,000^{\circ}\text{K.}$ , has not been accurately determined.

### Summary

Extreme low temperatures are needed to provide information about energy transformations useful in the study of thermodynamics and atomic structure. They are also used in the production and purification by fractionation of industrially important gases. Low temperatures are obtained practically by processes utilizing (1) adiabatic expansion of a gas with performance of mechanical work, (2) controlled expansion of a gas utilizing the Joule-Thomson effect, and (3) adiabatic demagnetization. Temperatures are measured by resistance thermometers to  $14^{\circ}\text{K.}$ , by helium thermometers as low as  $0.7^{\circ}\text{K.}$  and in terms of paramagnetic susceptibilities to yet lower limits.

High temperatures are necessary in the preparation and in controlling the properties of metallurgical and ceramic materials. The useful temperatures attained by flames, electric resistance electric arc and radiation furnaces are limited chiefly by the refractory materials available and the uniformity and control required. Optical pyrometer measurements based on the radiation laws are possible to the highest attainable temperatures.

**References**

- Crawhall, T. C. *Very low temperatures* . . . , London: H. M. Stationery Office, 1936.
- Dixit, K. R. "Production and Measurement of Low Temperatures," *Current Science*, 12, 589 (1938).
- Giauque, W. F. and MacDougall, D. P. "Thermodynamic Temperature Scale below 1°K.," *J. Am. Chem. Soc.*, 60, 376-88 (1938).
- Jackson, L. C. *Low Temperature Physics*, London: Methuen & Co., 1935.
- Ruhemann, M. and B. *Low Temperature Physics*, London: Cambridge U. Press, 1938.
- Cohn, W. M. "The Field of Extreme Temperatures," *Temperature—Its Measurement and Control* . . . New York: Reinhold. (1941) pp. 764-772.
- Walden, L. "The Construction of Laboratory Electric Furnaces . . . ," *J. Sci. Instruments*, 16, 1-9 (1939).

## CHAPTER XV

# The International Temperature Scale

## Scale Adopted in 1927, 1933

### Introduction

The Kelvin scale is recognized as the fundamental scale to which all temperatures should ultimately be referable. There is considerable experimental difficulty in the measurement of temperature on any thermodynamic scale. This led to the adoption in 1927 by the Seventh General Conference of Weights and Measures, representing 31 nations, of a practical scale which was designated the international temperature scale.<sup>1</sup> This scale agreed with the thermodynamic centigrade scale as closely as possible for the knowledge then available. It specified (i) the values for the fixed temperatures at which instruments are to be calibrated, (ii) the types of instruments to be used in realizing the scale, (iii) the equations to be used for interpolating or extrapolating from fixed points, and (iv) the experimental procedures recommended.

When a temperature  $t$  on the international temperature scale is expressed on the Kelvin scale, the relation  $T = t + T_0$  is used.  $T_0$ , the temperature of the normal freezing point of water, is found by experiment to be approximately 273°K. Temperatures expressed on the international temperature scale are ordinarily designated "°C.," but may be designated "°C. (int. 1927)" whenever necessary to avoid ambiguity.

### Fixed points

The scale is based upon a number of reproducible equilibrium temperatures or fixed points to which numerical values

<sup>1</sup> G. K. Burgess, *Bur. Standards J. Research* 1, 635 (1928).

are assigned. The basic fixed points are given in Table I for a pressure of one standard atmosphere, together with formulas which represent the temperature  $t_p$  as a function of the vapor pressure  $p$  over the range from 680 to 780 mm. of mercury.

The international temperature scale is important because it provides a definite, reproducible way of measuring and designating temperatures. It is not primarily concerned with the "correctness" of the temperatures so measured.

TABLE I  
BASIC FIXED POINTS

(For a pressure of  $1.01325 \times 10^6$  dynes/cm.<sup>2</sup>, which corresponds to a barometric height of 760 mm. at 0°C. for  $g = 980.665$  cm./sec.<sup>2</sup>)  
°C.

Temperature of equilibrium between liquid and gaseous oxygen (oxygen point).....	-182.97
$t_p = t_{760} + 0.0126(p - 760) - 0.0000065(p - 760)^2$	
Temperature of equilibrium between ice and air-saturated water (ice point).....	0.000
Temperature of equilibrium between liquid water and its vapor (steam point).....	100.00
$t_p = t_{760} + 0.0367(p - 760) - 0.000023(p - 760)^2$	
Temperature of equilibrium between liquid sulphur and its vapor (sulphur point).....	444.60
$t_p = t_{760} + 0.0909(p - 760) - 0.000048(p - 760)^2$	
Temperature of equilibrium between solid silver and liquid silver (silver point).....	960.5
Temperature of equilibrium between solid gold and liquid gold (gold point).....	1063.

### Interpolation

The means available for interpolation lead to a division of the scale into four parts.

(a) *From 0° to 660°C.* the temperature  $t$  is defined by the formula

$$R_t = R_0(1 + At + Bt^2) \quad (1)$$

where  $R_t$  is the resistance, at temperature  $t$ , of a platinum resistor, between the branch points formed by the junctions

of the current and potential leads of a standard resistance thermometer. The constants  $R_0$ ,  $A$  and  $B$  are calculated from measured values of  $R_t$  at the ice, steam and sulphur points. For a standard resistance thermometer the ratio  $R_{100}/R_0$  shall not be less than 1.390 and  $R_{444.6}/R_0$  shall not be less than 2.645.

(b) From  $-190^\circ$  to  $0^\circ\text{C}$ . the temperature  $t$  is defined by the formula

$$R_p = R_{760}\{1 + At + Bt^2 + C(t - 100)t^3\} \quad (2)$$

where the constant  $C$  is calculated from the measured value of  $R_t$  at the oxygen point after  $R_0$ ,  $A$  and  $B$  have been determined as in (a). A standard thermometer for use below  $0^\circ\text{C}$ . must in addition satisfy the requirement  $R_{-182.97}/R_0 \leq 0.250$ .

(c) From  $660^\circ$  to  $1063^\circ\text{C}$ . the temperature  $t$  is defined by the formula

$$e = a + bt + ct^2 \quad (3)$$

where  $e$  is the e.m.f. of a standard Pt-90Pt10Rh thermocouple when one junction is at  $0^\circ\text{C}$ . and the other is at temperature  $t$ . The constants  $a$ ,  $b$  and  $c$  are determined by calibration at the antimony, silver and gold points. The freezing point of the antimony employed is determined by use of a standard resistance thermometer. The platinum of a standard thermocouple shall be of such purity that  $R_{100}/R_0 \geq 1.390$ .

(d) Above  $1063^\circ\text{C}$ . the temperature  $t$  is defined by the formula

$$\log_e \frac{J_t}{J_{1063}} = \frac{c_2}{\lambda} \left[ \frac{1}{1336} - \frac{1}{(t + 273)} \right] \quad (4)$$

where  $\lambda$  is some wavelength, in cm., of the visible spectrum and  $J_t$  is the radiant energy (of wavelength  $\lambda$ ) per unit wavelength interval, emitted per unit time by unit area of a black-body at temperature  $t$ . The constant  $c_2$  is taken as 1.432 cm. deg. Eq. 4 is valid if  $\lambda(t + 273)$  is less than 0.3 cm. deg.

## Secondary points

In addition to the basic fixed points, the temperatures of a number of other points are available and may be used in the calibration of secondary temperature measuring

TABLE II  
SECONDARY POINTS

	°C.	
	Int. 1927	Int. 1939, proposed
Temperature of equilibrium between solid carbon dioxide and its vapor.....	-78.5	-78.51
$t_p = t_{760} + 0.1443(t_p + 273.2) \log \left( \frac{p}{760} \right)$ (1927)		
$t_p = t_{760} + 15.95 \left( \frac{p - 760}{1000} \right) - 11 \left( \frac{p - 760}{1000} \right)^2$ (1939)		
Temperature of freezing mercury.....	-38.87	-38.86
Temperature of transition of sodium sulphate decahydrate.....	32.38	32.38
Temperature of condensing naphthalene vapor.....	217.96	217.96
$t_p = t_{760} + 0.208(t_p + 273.2) \log \left( \frac{p}{760} \right)$ (1927)		
$t_p = t_{760} + 58.4 \left( \frac{p - 760}{1000} \right) - 33 \left( \frac{p - 760}{1000} \right)^2$ (1939)		
Temperature of freezing tin.....	231.85	231.85
Temperature of condensing benzophenone vapor....	305.9	305.9
$t_p = t_{760} + 0.194(t_p + 273.2) \log \left( \frac{p}{760} \right)$ (1927)		
$t_p = t_{760} + 64.2 \left( \frac{p - 760}{1000} \right) - 37 \left( \frac{p - 760}{1000} \right)^2$ (1939)		
Temperature of freezing cadmium.....	320.9	320.9
Temperature of freezing lead.....	327.3	327.3
Temperature of freezing zinc.....	419.45	419.5
Temperature of freezing antimony.....	630.5	630.5
Temperature of freezing copper in a reducing atm...	1083.	1083.1
Temperature of freezing nickel.....		1453.5
Temperature of freezing palladium.....	1555.	1552
Temperature of freezing platinum.....		1770
Temperature of freezing iridium.....		2446
Temperature of melting tungsten.....	3400	3390

instruments. These points and their temperatures on the international scale are listed in Table II. The temperatures given correspond to a pressure of one standard atmosphere. The formulas for the variation of equilibrium temperature with pressure are valid for the range from 680 to 780 mm.

## Revision of the International Temperature Scale

### Introduction

"It is expected that international thermometric conferences will be called, as occasion requires, by the International Committee on Weights and Measures, so that this temperature scale may be revised as the need arises."<sup>1</sup> Minor changes in the international temperature scale were adopted in 1933. More extensive changes were planned in 1939, but these did not progress beyond a report of the Advisory Committee on thermometry recommending their adoption by the International Committee on Weights and Measures.<sup>2</sup>

The Advisory Committee considered that it was inadvisable to make changes of a provisional nature or to change the scale appreciably at too frequent intervals. Hence it recommended "only the modifications judged strictly necessary under present conditions, or which could be considered as improvements in technic which did not affect the basis of the scale." The Committee enumerated the following questions which remain to be studied in anticipation of an eventual general revision of the international temperature scale:

- (1) Definition of the fundamental interval of the scale.
- (2) Substitution of the triple point of water for the melting point of ice.
- (3) Replacement of the thermocouple by the platinum resistance thermometer in the region 630.5 to 1063°C.
- (4) Revision of the value of the constant  $c_2$ . It was recognized that the value 1.436 cm. deg. is probably more exact than the value 1.432.

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<sup>2</sup> "Premier rapport du Comité Consultatif de Thermométrie au Comité International des Poids et Mesures," *Procès Verbaux du Bureau International des Poids et Mesures* [quoted from galley proofs].

Nature 145, 597 (1940).



Since in the temperature range now covered by the international temperature scale the difference introduced by this modification of the constant does not exceed the uncertainty of determinations of temperature, it seemed preferable to defer any change until additional experimental evidence is available for the true value of  $c_2$ .

### Fixed points

The scale proposed in 1939 defines the values of the fundamental fixed points as the same as those in Table I. The secondary fixed points recommended are listed in Table II. The Kelvin temperature of the ice point, not defined in 1927, is taken as  $273.15 \pm .02^\circ\text{K}$ .

### Interpolation

(a) From the ice point to the antimony point (0 to  $630.5^\circ\text{C}$ .) the temperature  $t$  is defined by Eq. 1, applied to a platinum resistance thermometer for which  $R_{100}/R_0 \geq 1.391$  and  $R_{444.6}/R_0 \geq 2.647$ .

(b) From  $-190^\circ\text{C}$ . to the ice point the temperature  $t$  is defined by Eq. 2, applied to a platinum thermometer which satisfies the conditions of (a) and in addition has  $R_{182.97}/R_0 \times 0.247$ .

(c) From the antimony point to the gold point ( $630.5$  to  $1063^\circ\text{C}$ .) the temperature  $t$  is defined by Eq. 3, applied to a standard Pt-90Pt10Rh thermocouple. The platinum of the couple shall be of such purity that  $R_{100}/R_0 \geq 1.1391$ . The couple shall develop an e.m.f. of between 10,200 and 10,400 microvolts with its junctions respectively at the ice and gold points.

(d) Above the gold point ( $1063.0^\circ\text{C}$ .) the temperature  $t$  is defined by the formula

$$\frac{J_t}{J_{1063.0}} = \frac{e^{\frac{c_2}{1336.15^\circ\text{K}} - 1}}{e^{\frac{c_2}{(t+273.15^\circ)\text{K}} - 1}} \quad (5)$$

in which  $c_2$  has the value 1.432 cm. deg.

Recommended Experimental Procedure  
and Supplementary Information

The equilibrium temperature between a liquid and its vapor varies markedly with pressure. Formulas representing the relation between pressure and equilibrium temperature are available. Since these formulas are not exact, it is desirable that when calibrating instruments at fixed points the equilibrium temperature realized experimentally approximate the one defined in Table I.

*The oxygen point* is best realized experimentally by the static method. The standard resistance thermometer and the free surface of the liquid oxygen in its container are brought to the same temperature in a suitable cryostat such as a well-stirred bath of liquid oxygen which need not be of high purity. The equilibrium temperature  $t_p$  corresponding to a pressure of  $p$  mm. of mercury may be found to an accuracy of a few thousandths of a degree, over the range of 680 to 780 mm., by means of the formula

$$t_p = t_{760} + 12.6 \left( \frac{p - 760}{1000} \right) - 6.5 \left( \frac{p - 760}{1000} \right)^2$$

*The ice point* is readily realized in a mixture of finely divided ice and pure water saturated with air at a pressure of one standard atmosphere. The effect of an increase in pressure is to lower the freezing point 0.007°C. per atmosphere.

*The steam point* is most readily realized by the dynamic method, with the thermometer in the condensing vapor. If the pressure of the vapor is transmitted to the manometer by means of air, the design of the hypsometer should take account of the fact that the density of air is greater than that of water vapor. If pressure is transmitted by means of helium, a hypsometer consisting of an insulated glass tube closed at the lower end and heated from below, with an ice-cooled condenser above and with the addition of a radiation

shield similar to that recommended for use in calibrations at the sulphur point, has been found very satisfactory.

The equilibrium temperature  $t_p$  may be found to an accuracy of about  $0.001^\circ\text{C.}$  over the range 660 to 860 mm. by means of either of the following formulas. The second is to be preferred to use outside the range mentioned.

$$t_p = t_{760} + 36.8578 \left( \frac{p - 760}{1000} \right) - 20.159 \left( \frac{p - 760}{1000} \right)^2 + 16.21 \left( \frac{p - 760}{1000} \right)^3$$

$$t_p = \frac{326}{1 - 0.197864 \log \frac{p}{760}} - 226$$

*The sulphur point* for resistance thermometer calibration is realized by adherence to the following specifications relating to purity of sulphur, boiling point apparatus, radiation shield and procedure.

The sulphur shall not contain more than 0.02% of impurities. Selenium is the impurity most likely to be present in quantities sufficient to affect significantly the equilibrium temperature.

The sulphur is contained in a tube of glass, fused silica or similar material, which has an internal diameter of from 4 to 6 cm. The tube is long enough so the vapor column accommodates the radiation shield and permits the required vertical displacement of the resistance thermometer. Electric heating is preferable. The source of heat and all material of high thermal conductivity in contact with it should terminate at least 4 cm. below the free surface of the liquid sulphur. Above the source of heat a suitable length of tube is surrounded with a heat-insulating material. Any device used to close the top of the tube should have an opening for free equalization of pressure.

The cylindrical radiation shield may be made of graphite or sheet metal with blackened inner surface. It should

extend at least 1.5 cm. beyond each end of the platinum resistor. The shield is open at the bottom and has a conical portion at the top which fits closely to the thermometer protecting tube.

In standardizing a thermometer the heating of the sulphur is so regulated that the line of condensation is at least 1 cm. above the top of the heat insulating material. The thermometer with its radiation shield is inserted into the vapor. The bottom of the shield should be not less than 6 cm. above the free surface of the liquid sulphur, and its top not less than 2 cm. below the top of the heat-insulating material surrounding the container. When the line of condensation has again reached the required level, simultaneous readings are made of resistance and pressure. The thermometer should then be displaced vertically, by at least the length of the platinum coil, and its resistance should not change by more than the equivalent of  $0.01^{\circ}\text{C}$ .

The equilibrium temperature  $t_p$  may be found to an accuracy of a few thousandths of a degree, over the range from 660 to 860 mm., from the formula

$$t_p = t_{760} + 90.8028 \left( \frac{p - 760}{1000} \right) - 47.573 \left( \frac{p - 760}{1000} \right)^2 + 43.61 \left( \frac{p - 760}{1000} \right)^3$$

*The silver and gold points* will probably not be changed by more than  $0.1^{\circ}\text{C}$ . if the metallic impurities likely to be present do not exceed 0.01 % for silver or 0.005 % for gold. For standardizing a thermocouple, the metal is contained in a crucible of pure graphite, refractory porcelain or other material which will not contaminate it appreciably. Silver must be protected from access of oxygen while heated. The metal is heated in an electric furnace to a few degrees above its melting point. The thermocouple, mounted in a porcelain tube with porcelain insulators separating the two wires, is inserted in the molten metal through a hole in the center of

the crucible cover. The metal is allowed to cool slowly. The depth of immersion should be such that the observed e.m.f. of the thermocouple is not changed by more than 1 microvolt when the immersion is increased or decreased by 1 cm. During freezing, the e.m.f. should remain constant within 1 microvolt for at least 5 minutes. As an alternative to displacing the couple, as a means of testing the absence of the influence of external conditions upon the observed e.m.f., both freezing and melting points may be observed. If these do not differ by more than 2 microvolts, the observed freezing point may be considered satisfactory.

*The freezing point of antimony*, when used for calibration, requires a procedure similar to that specified for silver. Antimony has a marked tendency to undercool before freezing. This will be minimized if the metal is heated only a few degrees above its melting point and if the liquid metal is stirred.

*The standard resistance thermometer* should be so constructed that the wire will be subjected to a minimum of mechanical constraint, in order that dimensional changes accompanying change of temperature may result in a minimum of mechanical stress being imposed upon the platinum wire. It is advisable to use platinum wire not smaller than 0.05 mm. or larger than 0.5 mm. in diameter for the resistor. The completed thermometer should be annealed at a temperature not lower than 450°C., if it is not to be used above the sulphur point, or in any case at a temperature not lower than the highest temperature at which it is to be used.

For convenience in computation Eq. 1 may be put in the Callendar form, Eq. 4, Chap. VII. Similarly Eq. 2 may be written as

$$t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left( \frac{t}{100} - 1 \right) \frac{t}{100} + \beta \left( \frac{t}{100} - 1 \right) \left( \frac{t}{100} \right)^3 \quad (6)$$

*The standard thermocouple* is preferably made of wire not less than 0.35 mm. or more than 0.65 mm. in diameter.

## Summary

The international temperature scale specifies the procedure to be followed in measuring temperature in order to yield values which are reproducible and internationally comparable over the range  $-190$  to about  $4300^{\circ}\text{C}$ . Values are assigned to selected fixed points, instruments (thermocouple, resistance thermometer and optical pyrometer) are specified to be calibrated at these fixed points, and the forms of equations for obtaining values other than the fixed points are defined. The scale adopted in 1927 agreed with the thermodynamic centigrade scale as closely as possible with the knowledge then available. The practical importance of the I.T.S. is the reproducibility of its values rather than their ultimate accuracy. Hence it is not desirable to make modifications in the I.T.S. which have only a provisional character or to change the scale appreciably at too frequent intervals.

## Problems

1. Taking the density of mercury at  $0^{\circ}\text{C}$ . as  $13.6961 \text{ gm. cm.}^{-3}$  and  $g = 980.665 \text{ cm. sec.}^{-2}$ , find the value of the standard atmosphere of pressure in dynes  $\text{cm.}^{-2}$
2. The freezing point of a sample of aluminum is indicated as  $659.87^{\circ}\text{C}$ . using a standard thermocouple, and as  $660.01^{\circ}\text{C}$ . using a standard resistance thermometer. What is the value of this temperature on the I.T.S.? Comment.
3. What are the limiting values of  $\delta$  for a standard resistance thermometer?
4. Compare the merits of the following procedures to be followed as precision of temperature measurements increases:
  - (i) The ice and steam points to be defined as  $0.0000^{\circ}\text{C}$ . and  $100.0000^{\circ}\text{C}$ . respectively.
  - (ii) The ice point to be defined as  $273.165^{\circ}\text{K}$ .



## PART II

# Experiments

### EXPERIMENT 1

## Gas Thermometer

### Object

Determination of the coefficient of expansion of a gas at constant volume. Use of a gas thermometer to measure an unknown temperature.

### Apparatus

Gas thermometer. Ice and steam baths. Cathetometer. Barometer. Sodium sulphate.

### Discussion

If a gas under constant pressure has a volume  $v_0$  at  $0^\circ\text{C}.$ , its volume  $v_t$  at any other temperature  $t$  is given by  $v_t = v_0(1 + \alpha t)$ , where  $\alpha$  is the coefficient of expansion of the gas. If instead the volume is kept constant a similar equation holds for pressure:  $p_t = p_0(1 + \alpha t)$ . At constant temperature, Boyle's law holds:  $p v = p_0 v_0$ . Hence, combining these expressions, the state of a gas may be defined completely by

$$p v = p_0 v_0 (1 + \alpha t) \quad (1)$$

In general Eq. 1 is only approximately true. A gas which obeys it strictly is called an ideal gas. Replacing  $\alpha$  by  $\frac{1}{273}$ , the coefficient of expansion of an ideal gas, and setting  $273 + t = T$  leads to

$$pv = (273 + t) \frac{p_0 v_0}{273} = R(273 + t) = RT$$

$T$  is called the absolute temperature.  $R$  is the gas constant.

The normal gas thermometer serves as the primary instrument for determining temperature on the thermodynamic temperature scale. For practical reasons, a constant volume gas thermometer is usually employed. Ideally, an unknown temperature  $t$  could be measured with such a thermometer by using the relation

$$t = \frac{p_t - p_0}{\alpha p_0} \quad (2)$$

For precision temperature measurements Eq. 2 must be used with certain corrections, two of which will be considered in this experiment.

The capillary connecting the thermometer bulb to its manometer (Fig. 151) is a so-called dead space or pressure-transmitting volume in which the gas is at a temperature which differs from that in the bulb. Let  $v_1$  be the volume of the bulb at temperature  $t$ , and let  $v_2$  be the volume of the capillary at  $t_1$ . Then

$$t = \frac{\alpha(p_t - p_0)}{p_0} \frac{v_1(1 - \alpha t_1) + v_2}{v_1(1 + \alpha t_1) - \alpha t v_2} \quad (3)$$

Further, it is necessary to take account of the change in volume of the glass bulb. If  $\gamma$  is the cubical coefficient of expansion of the glass, Eq. 2 becomes

$$t = \frac{p_1 - p_0}{\alpha(p_0 - \gamma p_1)} \quad (4)$$

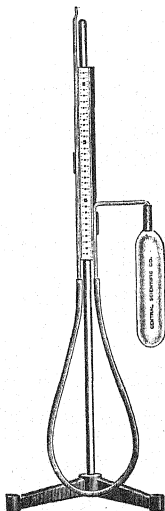


FIG. 151.—Gas thermometer. (Central Scientific Co.)



and Eq. 3 becomes

$$t = \frac{p_1 - p_0}{\alpha p_0 - \gamma p_1} \frac{v(1 + \alpha t_1) + v_2}{v_1(1 + \alpha t_1) - \alpha v_2} \quad (5)$$

The gas thermometer is calibrated conveniently by measuring  $p_0$  and  $p_{100}$  at the ice and steam points, respectively. An unknown temperature can be measured in terms of the corresponding pressure  $p_1$ :

$$t = \frac{100(p_1 - p_0)}{p_{100} - p_0} \left\{ 1 - \frac{p_{100} - p_1}{p_0} \left( \frac{\gamma}{\alpha} + \frac{v_2}{v_1(1 + \alpha t_1)} \right) \right\} \quad (6)$$

### Procedure

Surround the thermometer bulb with a mixture of cracked ice and water. When the gas has reached temperature equilibrium, measure  $p_0$  which may be expressed as the barometric height plus the difference in the heights of the left and right mercury columns of the manometer. Next circulate steam around the bulb and measure  $p_{100}$ . The steam temperature is obtained most accurately by reading a barometer and consulting steam tables for the corresponding boiling point. Use  $p_0$  and  $p_{100}$  to calculate  $\alpha$ .

Use the gas thermometer which you have calibrated to measure an unknown temperature. A check may be obtained on this work if a reproducible temperature, such as the transition temperature of  $\text{Na}_2\text{SO}_4$ , is measured.

## EXPERIMENT 2

### Coefficient of Expansion of a Liquid

#### Object

Measurement of the absolute coefficient of expansion of a liquid by the method of balanced columns.

#### Apparatus

Dulong and Petit type of liquid expansion apparatus. Boiler and burner. Barometer. Thermometer. Cathetometer or meter stick.

### Discussion

If a liquid has a volume  $V_0$  at  $0^\circ\text{C.}$  and  $V_t$  at  $t^\circ\text{C.}$ , the relation between volume and temperature may be expressed, to a good approximation, by the equation:

$$V_t = V_0(1 + \beta t) \quad (1)$$

$\beta$  is characteristic of the liquid and is called the coefficient

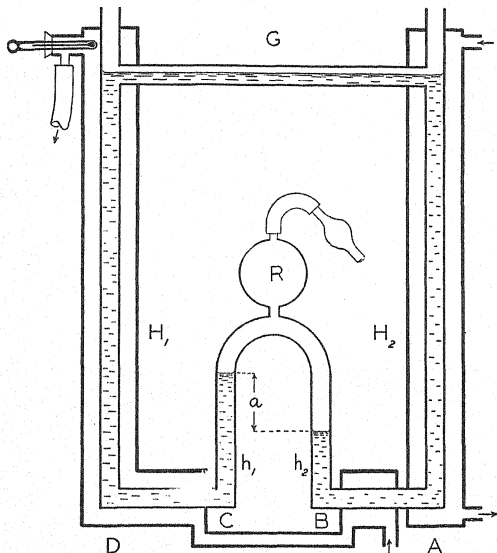


FIG. 152.—Hydrostatic balance method of measuring liquid expansion.

of cubical expansion. Solving Eq. 1 for  $\beta$ , it is seen that the coefficient of expansion represents the fractional change in volume per degree Centigrade:

$$\beta = \frac{v_t - v_0}{v_0} \quad (2)$$

and Eq. 3 becomes

$$t = \frac{p_1 - p_0}{\alpha p_0 - \gamma p_1} \frac{v(1 + \alpha t_1) + v_2}{v_1(1 + \alpha t_1) - \alpha t v_2} \quad (5)$$

The gas thermometer is calibrated conveniently by measuring  $p_0$  and  $p_{100}$  at the ice and steam points, respectively. An unknown temperature can be measured in terms of the corresponding pressure  $p_1$ :

$$t = \frac{100(p_1 - p_0)}{p_{100} - p_0} \left\{ 1 - \frac{p_{100} - p_1}{p_0} \left( \frac{\gamma}{\alpha} + \frac{v_2}{v_1(1 + \alpha t_1)} \right) \right\} \quad (6)$$

### Procedure

Surround the thermometer bulb with a mixture of cracked ice and water. When the gas has reached temperature equilibrium, measure  $p_0$  which may be expressed as the barometric height plus the difference in the heights of the left and right mercury columns of the manometer. Next circulate steam around the bulb and measure  $p_{100}$ . The steam temperature is obtained most accurately by reading a barometer and consulting steam tables for the corresponding boiling point. Use  $p_0$  and  $p_{100}$  to calculate  $\alpha$ .

Use the gas thermometer which you have calibrated to measure an unknown temperature. A check may be obtained on this work if a reproducible temperature, such as the transition temperature of  $\text{Na}_2\text{SO}_4$ , is measured.

## EXPERIMENT 2

### Coefficient of Expansion of a Liquid

#### Object

Measurement of the absolute coefficient of expansion of a liquid by the method of balanced columns.

#### Apparatus

Dulong and Petit type of liquid expansion apparatus. Boiler and burner. Barometer. Thermometer. Cathetometer or meter stick.

### Discussion

If a liquid has a volume  $V_0$  at  $0^\circ\text{C}.$  and  $V_t$  at  $t^\circ\text{C}.$ , the relation between volume and temperature may be expressed, to a good approximation, by the equation:

$$V_t = V_0(1 + \beta t) \quad (1)$$

$\beta$  is characteristic of the liquid and is called the coefficient

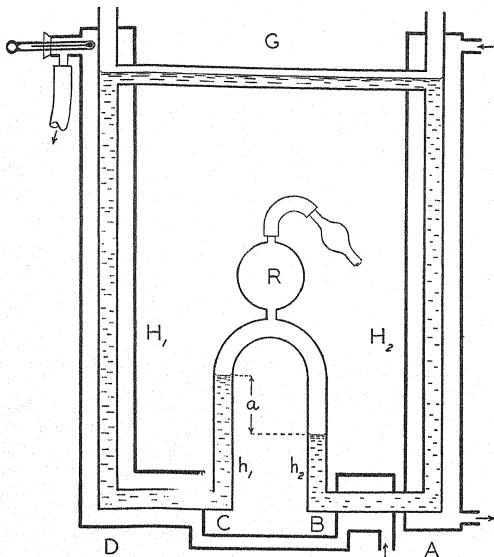


FIG. 152.—Hydrostatic balance method of measuring liquid expansion.

of cubical expansion. Solving Eq. 1 for  $\beta$ , it is seen that the coefficient of expansion represents the fractional change in volume per degree Centigrade:

$$\beta = \frac{v_t - v_0}{v_0} \quad (2)$$

The chief difficulty encountered in determining  $\beta$  experimentally is that the volume of the container as well as that of the liquid changes with temperature. This is overcome in a hydrostatic balance method first used by Dulong and Petit (1818) to measure the expansion of mercury, and improved in its present form by Regnault.

The liquid is contained in a tube, rectangular in outline, with an inverted U in the lower horizontal section (Fig. 152). Branch *A* is kept at a high temperature by means of a steam jacket. The rest of the apparatus is cooled to a uniform temperature by water jackets. The liquid columns *A* and *D* are connected at the top by tube *G* which equalizes the pressures in the columns at its level. The liquid surfaces in tubes *B* and *C* are separated by compressed air in reservoir *R*.

Let  $H_1$ ,  $H_2$ ,  $h_1$ ,  $h_2$  and  $a$  represent the differences in level indicated in the diagram. Denote the temperature and density of the liquid in column *A* by  $t_2$  and  $\rho_2$  respectively, and for the rest of the liquid by  $t_1$  and  $\rho_1$ . Let  $P$  be the atmospheric pressure and  $P'$  the pressure of air in *R*. The pressure at the base of column *D* is  $(P + \rho_1 g H_1)$  and at the base of column *C* is  $(P' + \rho_1 g h_1)$ . These are hydrostatic pressures at the same level in the liquid, hence

$$P + \rho_1 g H_1 = P' + \rho_1 g h_1 \quad (3)$$

In the same manner for columns *A* and *B*:

$$P + \rho_2 g H_2 = P' + \rho_1 g h_2 \quad (4)$$

Subtracting Eq. 4 from Eq. 3 and solving for  $\rho_1/\rho_2$ :

$$\frac{\rho_1}{\rho_2} = \frac{H_2}{H_1 - h_1 + h_2} = \frac{H_2}{H_1 - a} \quad (5)$$

where  $a$  has replaced  $(h_1 - h_2)$ .

The density of a given mass of liquid is inversely proportional to its volume. From Eq. 1:

$$\frac{\rho_0}{\rho_1} = \frac{V_1}{V_0} = 1 + \beta t_1 \quad (6)$$

$$\frac{\rho_0}{\rho_2} = \frac{V_2}{V_0} = 1 + \beta t_2 \quad (7)$$

On dividing Eq. 7 by Eq. 6, a value is obtained for  $\rho_1/\rho_2$ . If this value be equated to that in Eq. 5, and the resulting equation solved for  $\beta$ , one obtains:

$$\beta = \frac{a}{H_2(t_2 - t_1) - at_2} \quad (8)$$

### Procedure

Partially fill the apparatus by introducing the liquid at the top of column *A* or *D*. Compress air in reservoir *R* so that the liquid rises in tubes *A* and *D* until its surface stands about at the axis of tube *G*. Connect rubber tubing to circulate steam through the jacket on column *A* and tap water through the cooling jackets. Temperature  $t_1$  is read on a mercury thermometer. The temperature of the hot jacket is calculated from a barometer reading and steam tables. Measure  $H_2$  with a meter stick and  $a$  with a cathetometer. In calculating  $\beta$  use the mean of about five independent determinations of  $a$ .

In which type of apparatus would expansion of the container introduce a larger relative error: (a) a gas thermometer, (b) a liquid thermometer? Why?

## EXPERIMENT 3

### Rate of Cooling

#### Object

- (i) Investigation of the rate of cooling of a hot body.
- (ii) Comparison of cooling rates for polished and for black surfaces.
- (iii) Determination of the specific heat of liquid and solid naphthalene.
- (iv) Determination of the heat of

### Apparatus

Two calorimeters with a water jacket. Three metal tubes, or test tubes. Three thermometers. Bronze gauze. Water bath. Boiler. Burner. Timer. Balance. Beakers. Naphthalene.

### Discussion

A hot object in cooler surroundings loses heat by conduction, convection and radiation. Provided the temperature difference between the object and its surroundings is not very large, the process is described with considerable accuracy by Newton's law of cooling, which states that the *rate* at which heat is lost from the hot object is proportional to this difference in temperature. The actual rate of loss of heat will, of course, depend on the size, surface and surroundings of the object. For identical objects, like two identical cans, in the same surroundings, the rates of loss of heat are the same, as the cans, whatever their contents, are at the same temperature.

### Procedure

Fill a polished and a blackened tube with equal weights (estimated) of hot water, and suspend them from the cover of the laws-of-cooling apparatus, Fig. 153. Attach the cylindrical cans and immerse in the water jacket which is at room temperature. Push the bulbs of two thermometers through scraps of bronze gauze and place them in the two tubes. Take careful readings of each at one-minute intervals while the temperature falls over a range of about  $35^{\circ}\text{C}$ . The thermometers are most easily read if the observer faces the window. Find the mean temperature of the water jacket from observations taken at beginning and end of the cooling process. Plot two curves on the same sheet showing the cooling of the polished and the blackened tubes. Set the blackened tube aside for the rest of the experiment.

From a hot water bath take one tube of naphthalene and one of water when the temperature shown by their thermometers are above  $95^{\circ}\text{C}$ . These tubes should contain about equal quantities of liquid, as judged by eye. Dry the outside of each tube with one quick wipe with a towel, and set the tubes in the apparatus of Fig. 153, designed to provide constant temperature surroundings. Record the temperatures every minute until the tubes have cooled to about  $50^{\circ}\text{C}$ . The water will cool more rapidly. As soon as convenient, weigh the tube with water, then empty it and weigh again.

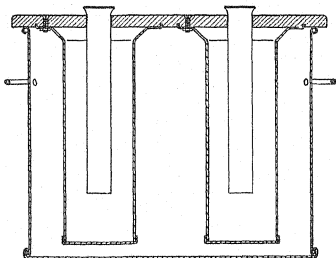


FIG. 153.—Laws of cooling apparatus. (Central Scientific Co.)

Put the empty test tube back into the water bath and let it heat to over  $95^{\circ}\text{C}$ . Then repeat the cooling process with the empty tube.

Represent the three series of observations on a graph sheet, drawing the curves to a large scale.

Let  $w$  = water equivalent of empty tube, in cal.  $\text{deg.}^{-1}$  C.

$w_1$  = water equivalent of naphthalene alone.

$w_2$  = water equivalent of water alone.

Also let  $p$ ,  $p_1$ ,  $p_2$  be the slopes (in  $\text{deg. C. min.}^{-1}$ ) of the three curves at some definite temperature,  $T_1$ . Then the rates of loss of heat in the three cases are, at temperature  $T_1$ ,  $wp$ ,  $(w + w_1)p_1$ ,  $(w + w_2)p_2$  measured in cal.  $\text{min.}^{-1}$ .



Since the tubes are identical, and cool in the same surroundings, these rates of loss of heat must all be the same. Hence

$$wp = (w + w_1)p_1 = (w + w_2)p_2$$

Now  $w_2$  is known from the measurement of the weight of water used, and  $p$ ,  $p_1$  and  $p_2$  can be found graphically after drawing tangents to the curves at temperature  $T_1$ . Hence  $w_1$  can be found. From this, if the mass of naphthalene is known, the specific heat of naphthalene can be calculated.

The calculation outlined above should be carried through for the solid, and, if possible, for the liquid naphthalene.

To find the heat of fusion, first compute the rate of loss of heat of the water at the temperature at which naphthalene solidifies. All the time the liquid is freezing, it is at the same temperature, and is losing heat at the same rate. By noting the length of time the naphthalene takes to solidify, the total heat given out can be calculated. Then find the heat of fusion in calories per gram.

#### EXPERIMENT 4

## Properties of Air and the Psychrometric Chart

### Object

(A) Determination of the pressure-temperature curve of saturated water vapor. (B) Measurement of absolute and relative humidity. Comparison of several types of hygrometers.

### Apparatus

(A) Vapor pressure apparatus. Manometer. Barometer. Burner or electric heater. Aspirator. Bicycle pump. (B) Dew point hygrometer. Ether. Thermometer. Wet and dry bulb hygrometer, sling hygrometer, or aspiration hygrometer. Electric fan. Distilled water. Thermocouple materials. Potentiometer.

### Discussion

(4) It is the purpose of this experiment to observe the pressure exerted by saturated water vapor at different temperatures. For ordinary room temperatures this pressure is small (between 1 and 2 cm. Hg). As the temperature rises the vapor pressure rises at an increasing rate. The liquid boils when the pressure of its vapor equals the external pressure. For a given pressure the temperature of the boiling liquid remains constant as long as there is any liquid to vaporize.

Figure 154 illustrates apparatus for determining the pressure-temperature curve of saturated water vapor by the dynamic method. Water is boiled and the vapor condensed in a closed system in which the pressure may be varied. As water is boiled in the pyrex flask, the vapor passes up into the condenser where it is condensed by a stream of cold water. If it were not for the condenser the steam formed would increase the pressure in the boiler and thus change the boiling point. The temperature of the boiling liquid is read from a thermometer placed in the vapor. The vapor pressure is determined by adding to the observed barometric pressure the difference in the manometer readings (open tube minus closed tube levels). A reservoir between the condenser and the mercury

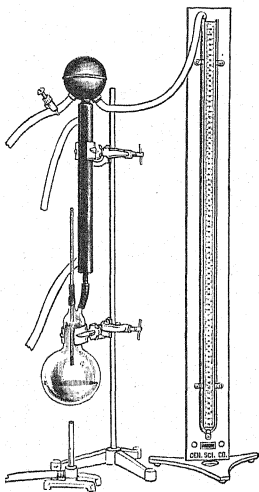


FIG. 154.—Vapor pressure apparatus.  
(Central Scientific Co.)

manometer serves to equalize any sudden changes of pressure due to irregularities in boiling.

(B) Human comfort, many scientific measurements and industrial processes are dependent on the maintenance of suitable climatic conditions. The condition of the atmosphere, aside from contamination, is determined by the temperature and the amount of moisture which it contains. There are a variety of ways of describing the moisture content of the air:

*Absolute humidity* (vapor density) is the mass of water vapor present in unit volume.

The *pressure of water vapor* present in the atmosphere varies up to a maximum or saturation value, which is found to depend on the temperature.

*Relative humidity* is usually defined in meteorology as the ratio of the mass of water vapor actually present in unit volume to that contained in a unit volume when the atmosphere is saturated; in the other sciences as the ratio of the corresponding pressures of water vapor.

The *dew point* is the temperature at which water vapor becomes saturated.

Absolute humidity is measured by absorbing physically or chemically the amount of water in the form of vapor in a given volume. The equipment necessary is somewhat elaborate and the method requires time and very exact observations.

A common empirical method, frequently employed in household instruments, is to measure the change in length of a hygroscopic material, such as hair. Instruments of this type must be calibrated by an absolute method; and as the physical and chemical characteristics of hygroscopic substances are subject to change, frequent recalibration is necessary.

The most accurate method for determining the moisture content of air is a determination of the dew point, i.e., the highest temperature at which the water vapor present in the air is sufficient to give saturation. From a table of

the amount of water vapor required to saturate the air at different temperatures (see Exp. 4A and Table XXIV) the maximum amount of moisture at the dew point is read, and thus the actual water vapor content of the air is determined. The dew point hygrometer, Fig. 155, consists of a thin plate of highly polished metal on the rear side of which a cooling liquid flows. The temperature of the liquid is varied until moisture appears on the polished surface. The polished surface is preferably observed with a reading telescope. The temperature of the cooling liquid is varied between appearance and disappearance of the film and an average of the observed temperatures gives the dew point with high accuracy.

A more common device for humidity measurements is the wet and dry bulb hygrometer, Fig. 156, which, from temperatures and a semi-empirical formula, gives the relative humidity. The wet bulb is surrounded by a wick saturated with water.

Evaporation of the water from the wick absorbs heat from the wet bulb and lowers its temperature. The actual temperature of the wet bulb depends on the balance between heat lost and the heat received by conduction and radiation. The lower the relative humidity, the greater will be the evaporation and the lower the wet bulb temperature.

The air is never at rest and the wet-bulb temperature will fluctuate with air currents. If, however, the wet bulb

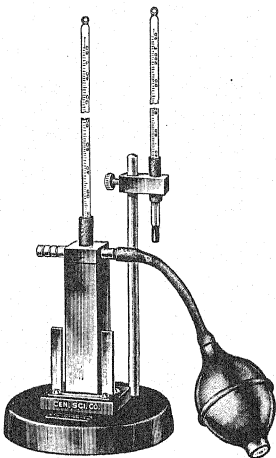


FIG. 155.—Alluard-type dew point hygrometer. (Central Scientific Co.)

is in an air stream its temperature becomes constant when the velocity is sufficient to remove the maximum water vapor evaporating from the wet bulb. With a proper wick an air velocity of 600 ft. per minute at normal atmospheric pressures gives the minimum wet-bulb temperature. This air velocity can be secured either by moving the wet bulb through the air (*sling psychrometer* Fig. 157) or by moving the air past the wet bulb (*aspiration psychrometer*). To secure similar conditions for both wet and dry bulbs, both have always the same relative air motion.

The formula for the wet-dry bulb hygrometer is

$$p_a = p_w - AB(t_d - t_w) \quad (1)$$

where  $p_a$  is the actual vapor pressure,

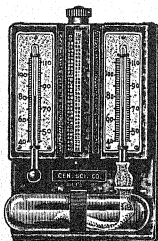


FIG. 156.—Wet and dry bulb hygrometer. (Central Scientific Co.)

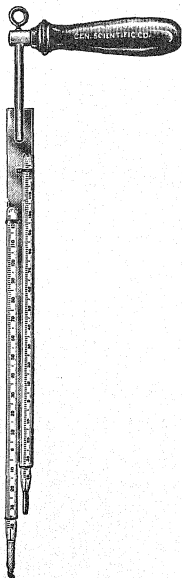


FIG. 157.—Sling psychrometer. (Central Scientific Co.)

$p_w$  the saturated vapor pressure at  $t_w$ ,  $B$  is the ratio of the actual barometric pressure to the standard value, and  $A$  a factor depending upon the access of heat to the bulbs by conduction and radiation. If  $p$  is in mm. Hg,  $t$  in  $^{\circ}\text{C}$ ., with an air flow of

3 meters per second, and a suitable wick is used,  $A$  for mercury-in-glass thermometers and thermocouples is about 0.00057. Access of heat to the wet bulb by conduction and radiation can be greatly reduced by diminishing the size of the temperature observing instrument. Less loss of heat by evaporation is then required and consequently the air velocity past the wet bulb may be decreased.

### Procedure

(A) Connect the reservoir of the vapor pressure apparatus to an aspirator. When the pressure in the system has reached the lowest limit that can be obtained conveniently, close the stopcock. (Never shut off the aspirator when the stopcock is turned so as to allow water to pass from the aspirator to the test of the system.) Test for leaks by noting whether the reading of the manometer remains constant.

Heat the water in the boiler and observe the thermometer as its readings increase until they finally become constant. Record this temperature and the corresponding manometer reading. Read the barometer. Calculate the pressure corresponding to the observed boiling point.

Change the pressure by allowing a little air to enter the system. Note and record the manometer and thermometer readings when the steady state has been reached. Continue these observations at about five different pressures until atmospheric pressure is reached.

Connect the system to a pressure pump and increase the pressure by about 15 cm. Hg, and continue readings at higher pressures until the mercury level in the closed tube is about 5 cm. from the bottom of the manometer.

Plot the observed boiling point vs. pressure curve. On the same sheet, plot a curve representing the data of Table XXIV.

(B) Make a quick, approximate determination of the dew point with the dew point hygrometer. Next make four sets of observations of the temperatures at which the dew

appears and disappears, allowing the temperature to change very slowly in the neighborhood of the point previously determined. Record the temperature of the room and the barometric height.

Using a wet and dry bulb hygrometer, sling psychrometer or aspiration psychrometer, follow the manufacturers directions as to ventilation and record the readings of both thermometers. Repeat in still air.

Construct a thermocouple hygrometer, using fine (No. 40) wires to make copper-constantan or nichrome-constantan junctions. The wick may be made of woolen or soft cotton yarn wound in a close single layer extending at least 1 cm. on each side of the junction with the ends dipping into a reservoir of distilled water. The dry junction should be above the wet junction and distant at least 2 cm. Compare the readings of this instrument when in still air and when in the air current from an electric fan.

Calculate the absolute humidity and the relative humidity of the laboratory as indicated by each of the instruments. Present the results in tabular form for comparison. Make a rough computation of the total amount of water present in the air of the room. Compare the instruments used as to accuracy, convenience and adaptability to remote reading and recording.

### Questions

(A) 1. Sketch and explain a simple manometer-type apparatus for determining the pressure-temperature curve for water vapor by a static method. Has this any advantage over the method used in this experiment?

2. If the liquid has boiled for some time in the apparatus of Fig. 153, boiling with "bumping" is likely to occur, especially at temperature lower than  $75^{\circ}\text{C}$ . Explain.

3. Discuss the variation of the boiling point of a liquid with pressure, from the standpoint of the kinetic theory of matter.

4. If the gage pressure of a locomotive be maintained constant, how will the power of the engine when the locomotive is at high altitude compare with its power at low levels?

(B) 1. When the relative humidity is 0.47 at  $21^{\circ}\text{C}.$ , what will be the dew point?

2. If the absolute humidity of the atmosphere on a certain day is  $13.5 \text{ gm. m.}^{-3}$  what is its relative humidity at  $22^{\circ}\text{C}.$ ? Assuming that the temperature drops to  $12^{\circ}\text{C}.$  that night, speculate on what may happen.

3. Is it necessary that the atmosphere next to the earth be saturated in order to have rain?

4. Is it correct to say a furnace *dries* the air in a home in the sense of lowering (appreciably) its absolute humidity? Does it lower its relative humidity?

5. How would one go about raising the humidity in a house heated by hot air? How much water would have to be evaporated to raise the relative humidity of a house of  $500 \text{ m.}^3$  from 20 to 50%, the temperature being  $22^{\circ}\text{C}.$ ?

6. Explain why cold surfaces are more likely to "sweat," i.e., show condensation, in summer than in winter.

7. Under what conditions may the wet bulb of a hygrometer indicate a higher temperature than the dry bulb?

## EXPERIMENT 5

### Thermoelectricity

#### Object

(i) Experimental verification of the thermocouple relations discussed in Chap. III (p. 48). (ii) Calibration of a chromel-alumel thermocouple, for the range  $0^{\circ}$  to  $450^{\circ}\text{C}.$  (iii) Determination of the thermoelectric power of various metals in combination with copper, for the range  $0^{\circ}$  to  $450^{\circ}\text{C}.$

#### Apparatus

A set of thermocouples made of copper in combination with each of the following: chromel, alumel, nichrome, con-



stantan and iron. A two-range student-type potentiometer. Materials with known boiling points: water, naphthalene, benzophenone and sulphur. Ice bath. Test tubes. Thermocouple protecting tubes.

### Discussion

This experiment illustrates the method of calibrating a thermocouple by measuring its e.m.f. at each of several fixed temperatures provided by pure materials of known boiling points. The chromel-alumel thermocouple chosen for calibration is commonly used for laboratory and industrial temperature measurements. The meaning and usefulness of the concept of thermoelectric power  $P$  is illustrated by calculating  $P$  for nichrome and constantan, each in combination with copper, from e.m.f. measurements.

When one junction of a thermocouple is held at constant temperature (usually  $0^{\circ}\text{C}.$ ) the variation of the thermal e.m.f. with temperature of the other junction is expressed by,

$$E = a + bt + ct^2 \quad (1)$$

Thermoelectric power  $P$  is defined as the change in thermoelectromotive force for unit change in temperature. Hence  $P$  may be obtained by differentiating Eq. 1:

$$P = \frac{dE}{dT} = b + 2ct \quad (2)$$

It will be observed that the e.m.f.-temperature relation is parabolic. The thermoelectric power-temperature relation is linear. The thermal e.m.f. is usually measured in millivolts, the thermoelectric power in microvolts per degree Centigrade.

Boiling points may be corrected for barometric pressure  $p$ , measured in millimeters of mercury, by the formulas,

Water	$t = 100.000 - 0.0367(760 - p)$
Naphthalene	$t = 217.96 - .058 (760 - p)$
Benzophenone	$t = 305.9 - .063 (760 - p)$
Sulphur	$t = 444.6 - .091 (760 - p)$

### Procedure

A student-type potentiometer with variable resistance  $R$ , standard cell  $SC$ , galvanometer  $G$ , and protective resistance  $P$  connected externally is indicated in Fig. 158. An understanding of this circuit, and the wiring diagram of the potentiometer will aid in the intelligent use not only of this instrument but also of more specialized, self-contained potentiometers used in later experiments. (The extra terminals,

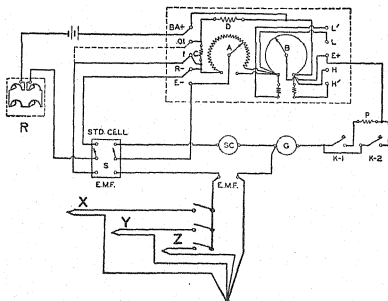


FIG. 158.—Potentiometer and thermocouples. (Potentiometer circuit by Leeds & Northrup Co.)

end coils and the red scale at  $B$  are to permit this instrument to be used as a Wheatstone bridge in other experiments.)

First standardize the current in the potentiometer circuit. To do this, throw switch  $S$  (Fig. 158) to the "Std. cell" position. Turn dial switch  $A$  and knob  $B$  until the potentiometer reading corresponds to the voltage of the standard cell being used. The adjustable resistor  $R$  in series with the battery should then be set at about 140 ohms to limit the current through the potentiometer to approximately 0.01 amp. Then tap key  $K-1$  and adjust resistor  $R$  to reduce any galvanometer deflection to zero. Make the final adjustment of  $R$  using key  $K-2$ , which gives increased galvanometer sensitivity. The switch  $S$  is then put in the "EMF" posi-

tion and the potentiometer is ready to make measurements. However, the current should be standardized occasionally during prolonged use. (Why?)

With the cold junction of one of the thermocouples in melting ice, measure carefully the e.m.f. when the hot junction is successively at the boiling points of water, naphthalene, benzophenone and sulphur. Use protecting tubes on the thermocouples, and avoid contaminating the samples by transferring protecting tubes from one to another. Avoid overheating the liquids.

Note the algebraic sign of the thermal e.m.f. as well as its magnitude. The sign is determined by observing the polarity at switch  $S$  and recalling the sign convention for a thermocouple:  $E_{ab}$  is positive when the positive or conventional current flows from  $a$  to  $b$  at the hot junction. For example, in Fig. 158  $E_{xcu}$  is positive (or  $E_{cux}$  negative). It may be found necessary to reverse the connections at  $S$  when another thermocouple is used, indicating  $E_{rcu}$  negative.

Repeat the foregoing for each of the couples.

Using the data for chromel-copper and alumel-copper couples, plot curves of e.m.f.'s as ordinates against corresponding temperatures as abscissas. On the same sheet, plot a curve of  $(E_{\text{Chromel-Cu}} - E_{\text{Alumel-Cu}})$  vs. temperature. By the second thermocouple relation, this should be a calibration curve for a chromel-alumel thermocouple. How may this be verified?

Check the first thermocouple relation by placing the cold junction of one of the thermocouples in the steam bath ( $t_2$ ) and the hot junction in boiling naphthalene ( $t_3$ ). Using previous e.m.f. readings taken with the cold junction in ice ( $t_1$ ), compare  $|E|_{t_1 t_3}$  with  $|E|_{t_1 t_2} + |E|_{t_2 t_3}$ .

What additional observation will permit checking the third thermocouple relations? If time permits carry this out.

Using the e.m.f.-temperature data for the nichrome-copper and the constantan-copper couples, plot graphs of thermo-

electric power vs. temperature. These may be obtained graphically from the slopes of the e.m.f.-temperature curves. Solve for constants  $b$  and  $2c$  of Eq. 2, for either one of these couples. Check your values by consulting tables which give these constants in combination with lead as a reference metal. (Note the sign convention employed in any tables you consult.)

In discussing the accuracy of this experiment, give numerical significance to your remarks by noting the least count of the potentiometer, its sensitivity (which depends upon the galvanometer) and the magnitude of random variations in measurements of a particular e.m.f.

1. When will  $a$  in Eq. 1 be zero and when different from zero?
2. Why is lead commonly used as a reference material in tabulating constants of thermoelectric power? What is the practical use of such tables?
3. List the three thermocouple relations in order of their practical importance.

## EXPERIMENT 6

### Comparison Method of Thermocouple Calibration

#### Instruments Used to Measure Thermal E.m.f.'s

##### Object

(i) Calibration of a base-metal thermocouple by comparison with a standard platinum vs. platinum-rhodium thermocouple. (ii) A study of instruments used in measuring thermocouple e.m.f.'s.

##### Apparatus

Standard platinum vs. platinum-rhodium thermocouple.  
Uncalibrated base-metal couple (chromel-alumel, copper-

constantan or iron-constantan). Electric furnace. Rheostat or variable transformer. Potentiometer. High-resistance millivoltmeter. Low-resistance millivoltmeter. Ice bath. Mercury thermometer. Three d.p.d.t. switches. Dry cell. Resistance dial box.

### Discussion

The primary standardization of a thermocouple is a calibration in terms of certain reproducible temperatures, obtained at the melting or freezing points of a series of pure metals. (See Exps. 7, 22.)

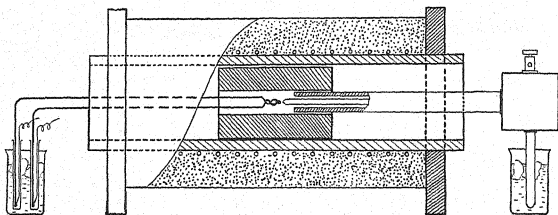


FIG. 159.—Comparison calibration of thermocouples.

A rapid, secondary calibration of a thermocouple, sufficiently accurate for most uses, may be obtained by comparison with a standard couple. If the two thermocouples are placed in a clean electric muffle furnace, readings of their e.m.f.'s may be taken conveniently over the temperature range for which calibration is required. To insure good thermal contact the rare-metal couple, without its protecting tube, may be pinched in a small slot cut in the hot junction of the base-metal couple; or both couples may be fused together temporarily. Obviously neither of these methods is practical for use in routine calibration of many couples. In this experiment good thermal contact is secured by inserting both couples in holes drilled in a small block of copper or nickel placed at the center of the furnace (Fig. 159).

It is just as important to know the temperature of the cold junction of the couple being calibrated as that of its hot junction. The thermal e.m.f. depends upon both. The reference junctions of each thermocouple may be placed in melting ice.

Or, if this is not done, a reference junction correction must be added to e.m.f. readings taken on the standard couple, and the calibration of the base-metal couple must include a statement of its reference junction temperature (measured with a mercury thermometer).

It is convenient, though not necessary, to use two potentiometers in this experiment. The relatively low e.m.f. produced by the platinum to platinum-rhodium couple may then be read on a low-range instrument (0-16 mv.) or on the lower scale of a multiple-range instrument. The e.m.f. produced by the base-metal couple is measured on a higher-range potentiometer (0-64 mv.).

Simultaneously with the calibration of the thermocouple, a study may be made of various e.m.f.-measuring instruments. A potentiometer will read the true e.m.f. of the couple, irrespective of lead resistance, since when balanced it takes no current from the couple. A millivoltmeter reading  $E_v$ , however, depends on the true e.m.f.  $E$  of the couple to which it is connected, the millivoltmeter resistance  $R_v$ , the thermocouple resistance  $R_c$  and the line resistance  $R_l$ ,

$$E_v = \frac{R_v}{R_v + R_c + R_l} E \quad (1)$$

### Procedure

Arrange the two thermocouples in the furnace with their hot junctions in the copper or nickel block. Close the ends of the furnace with insulating material. Provide an ice bath for the cold junction of each couple. Connect the standard couple to a potentiometer. Arrange switches to connect the base-metal couple to each of the instruments in turn.

Plan to obtain furnace temperatures from the standard couple at intervals of about  $100^{\circ}\text{C.}$  up to the highest temperature safe for the particular furnace and base-metal couple used. At each of the known furnace temperatures, record the e.m.f. of the base-metal couple as read on each of the three indicators. It is essential that the furnace temperature be kept constant during a set of readings by adjusting the heating current.

Draw a calibration curve (e.m.f. vs. temperature) for the base-metal couple.

Note what effect separating the thermocouples by several centimeters or removing the insulating plugs has on the e.m.f. readings. Estimate the temperature gradient encountered along the axis of the furnace. How might it be minimized?

Data taken so far will permit a qualitative check only of Eq. 1. If time permits, obtain from the instructor apparatus to measure  $R_1 + R_c$  and  $R_v$ . Use these values to verify Eq. 1 numerically.

1. Show how to estimate the accuracy of a comparison calibration of a thermocouple, considering: (i) the least count of the measuring instrument used, (ii) its sensitivity, (iii) any random variation of potentiometer readings at a given temperature and (iv) any change in readings noted when the thermocouples were moved slightly in the furnace.

2. What chiefly distinguishes a potentiometer from other e.m.f.-measuring instruments?

3. Derive Eq. 1 by applying Ohm's law to a thermocouple circuit.

4. Explain precisely the significance of a cold junction correction. Was it necessary in this experiment?

5. When both a platinum vs. platinum-rhodium and a base-metal thermocouple are used in the same furnace need any precaution be taken to prevent the furnace atmosphere damaging the couples? Explain.

6. Is it necessary or desirable that an electric muffle furnace used in thermocouple calibration be thermally well-insulated?

## EXPERIMENT 7

## Precision Calibration of a Thermocouple

**Object**

Graphical and analytical calibration of a thermocouple for the range 300° to 1100°C.

**Apparatus**

Thermocouple. Precision potentiometer. Electric timer. Electric furnace. Gas furnace. Crucibles. Quartz thermocouple protecting tubes. Powdered graphite. Samples of the following, three of which should be used: tin, lead, zinc, antimony, aluminum, sodium chloride and copper.

**Discussion**

The e.m.f.-temperature relation for a thermocouple may be represented by,

$$E = a + bt + ct^2 \quad (1)$$

where  $E$  is usually expressed in millivolts and  $t$  in degrees Centigrade. The constants  $a$ ,  $b$  and  $c$  are determined by measuring the thermocouple e.m.f. at the known melting points or freezing points of each of three metals.

The application of freezing point determinations to thermocouple standardization should be apparent from a consideration of Fig. 160. When a crucible of pure molten metal is allowed to cool, the curve obtained by plotting temperature of the metal against time is continuous until the freezing point is reached. During freezing the latent heat associated with the transformation supplies the losses due to radiation and conduction, and the temperature of the metal remains constant until all the metal has solidified. In that region the cooling curve is, ideally, parallel to the time axis. Actually there may be some obliquity of that part of the freezing curve, and to a greater degree also in the corresponding melting curve. On heating the latent heat of fusion is



wall of the crucible first reaches the melting point. The temperature of that layer remains constant while heat is supplied for its fusion. The thermocouple measures the temperature of the solid metal at the center of the crucible, and when this is surrounded by an isothermal layer the rate at which the inside temperature increases is greatly dimin-

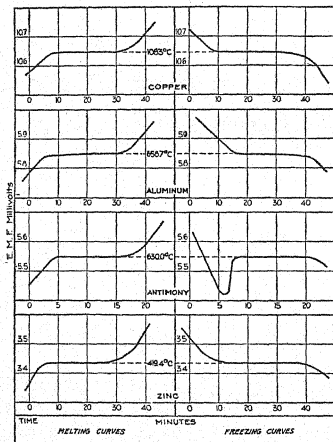


FIG. 160.—Typical heating and cooling curves. (Bur. Standards Tech. Paper 170.)

ished, resulting in a rounding off of the temperature-time curve. The thermocouple reads the true melting point only for the short time the metal immediately surrounding it is melting. Figure 161 shows a freezing and a melting curve with considerable obliquity. The true freezing temperature is obtained by extrapolating the straight portion of the curve and noting the temperature *A* at which the straight line deviates from the observed curve. The melting point *B* is

obtained from the last part of the melting curve in a similar way.

Undercooling in the case of most metals seldom exceeds  $0.1$  or  $0.2^{\circ}\text{C}$ . In the case of antimony, however, it may amount to as much as  $30^{\circ}\text{C}$ ., depending on the rate of cooling. The cooling curve for antimony in Fig. 160 illustrates undercooling.

### Procedure

The electric furnace should be turned on at the beginning of work and allowed to heat one of the samples while connections are made to the potentiometer. Have an instructor inspect the wiring before attempting to standardize the current through the potentiometer. Take a practice reading of the potentiometer with one junction of the thermocouple at room temperature, the reference junction being in ice.

When one of the samples has become molten, cover the surface with powdered graphite to retard oxidation. Insert a thermocouple protecting tube and then the couple. As the metal cools, take e.m.f. readings at intervals of 15 seconds and prepare a cooling curve of e.m.f. vs. time. The sample may be cooled in the furnace with power off or with the crucible in an asbestos-lined pot on the table. A uniform rate of cooling of about  $2^{\circ}\text{C}/\text{min}$ . from  $10^{\circ}\text{C}$ . above the melting point is satisfactory for a freezing point determination. The curve should have a flat portion corresponding to an interval of about 5 minutes.

With the exception of antimony, it is not advisable to stir the molten metals as pockets of graphite are thereby formed. If there is doubt concerning the proper depth of immersion of the thermocouple, several determinations of

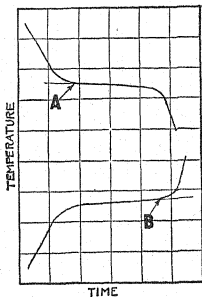


FIG. 161.—Oblique freezing and melting curves. (Bur. Standards Tech. Paper 170.)

## Temperature Measurement

its e.m.f. should be made at different depths until a position is found from which small variations do not affect the temperature measurement. The thermocouple protecting tube may be left in the metal for a few degrees below the freezing point without breaking. If it cannot then be removed, the metal should be remelted immediately. Time and material will be saved in obtaining freezing points if metals are not initially heated to unnecessarily high temperatures.

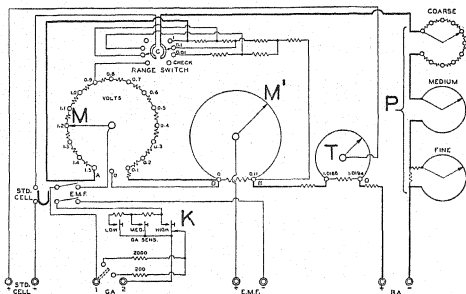


FIG. 162.—Circuit diagram of a "K-2" [Kohlrausch] potentiometer. (Leeds & Northrup Co.)

Submit with your report the three cooling curves and an accurate calibration for the thermocouple. Evaluate the constants  $a$ ,  $b$  and  $c$  of Eq. 1.

1. Draw a diagram of the simplest form of slide wire potentiometer.

2. Referring to Fig. 162, list those letters which designate elements essential to a simple potentiometer such as you have diagramed above.

3. List those parts which you have not included in (2) and explain in a phrase their function in the more elaborate instrument.

4. The current through a potentiometer has been standardized properly against a standard cell. If the following

changes are made, indicate whether restandardization is necessary:

- a.* The galvanometer is replaced by one of higher sensitivity.
- b.* Room temperature rises by about  $10^{\circ}\text{F}$ .
- c.* The thermocouple leads are lengthened, increasing their resistance.
- d.* Thermocouples of different metals are substituted.
- e.* The service cell is replaced by another.
- f.* The potentiometer range is changed from "1" to "0.1."

5. A potentiometer is standardized with the standard cell dial set at 1.0183 v. An unknown e.m.f. is then measured as  $X = 0.50915$  v. Later it is found that the correct standard cell e.m.f. was 1.0169 v. What then was the true value of  $X$ ?

6. A millivoltmeter connected to a thermocouple reads 14.286 mv. while a potentiometer connected to the same couple reads 15.000 mv. If the line and couple resistance is 2 ohms, find the resistance of the millivoltmeter.

## EXPERIMENT 8

### Thermal Conductivity of Heat Insulators

#### Object

Determination of the thermal conductivity of cork, glass, paper and several commercial insulating materials. Demonstration of the use of a differential thermocouple.

#### Apparatus

Fitch conductivity apparatus, consisting of source and receiver with embedded thermocouples. Constantan wire. 500-w. immersion heater. Galvanometer. Resistance box. Samples for test. Several kilogram weights.

### Discussion

In unidirectional heat flow the quantity of heat transferred by conduction is given by the equation:

$$Q = \frac{KA t(T_1 - T_2)}{L} \quad (1)$$

where  $Q$  = quantity of heat transferred, in calories.

$K$  = thermal conductivity, in c.g.s. units.

$A$  = area of cross section in  $\text{cm.}^2$

$L$  = distance between hot and cold faces, in cm.

$T_1, T_2$  = temperatures of hot and cold faces, respectively, on Centigrade scale.

$t$  = duration of heat transfer, in seconds.

In the case of good conductors, such as metals, the conductivity is measured from samples in the form of rods.

But for heat insulators, such as those investigated in this experiment, the length  $L$  must be small and the area  $A$  relatively large in order that sufficient heat transfer may occur to permit accurate measurement.

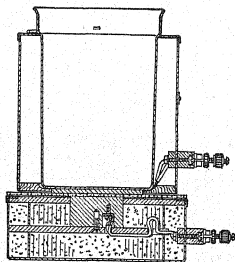


FIG. 163.—Fitch conductivity apparatus. (Central Scientific Co.)

The Fitch conductivity apparatus (Fig. 163) has as the heat source a vessel of boiling water and as a receiver a copper plug of known mass, embedded in insulating surroundings. The sample is placed between the polished faces of source and receiver.

The quantity of heat transferred is determined from the rise in temperature of the receiver, initially at room temperature. Copper-constantan thermocouples embedded in the bottom of the copper vessel (source) and in the receiver permit measurement of  $T_1$  and  $T_2$ . Losses from the copper

receiver by radiation and conduction to its surroundings are largely compensated for by the fact that the source has a larger area than the receiver, although the area used in computing  $K$  is that of the receiver.

A direct but rather laborious way of performing the experiment would be to measure the time rate of increase of  $T_2$ , after calibration of the thermocouple, and to compute  $Q$  from the thermal capacity of the receiver. An ingenious variation of this, however, simplifies the work.

Eq. 1 may be differentiated:

$$\frac{dQ}{dt} = \frac{KA(T_1 - T_2)}{L} \quad (2)$$

If  $M$  is the mass of the receiver and  $c$  the thermal capacity of copper:

$$\frac{dQ}{dt} = Mc \frac{dT}{dt} = \frac{KA(T_1 - T_2)}{L} \quad (3)$$

If now the constantan terminals of the two thermocouples are joined by constantan wire, the galvanometer deflection  $I_g$  will measure the temperature difference:

$$I_g = c'(T_1 - T_2) \quad (4)$$

and

$$\frac{dI_g}{dt} = -c' \frac{dT}{dt} \quad (5)$$

Substituting equations 4 and 5 in 3:

$$Mc \frac{dI_g}{dt} = - \frac{KA I_g}{L} \quad (6)$$

Integrating between the limits  $t = 0$  and  $t = t$ , corresponding to galvanometer deflections  $I_0$  and  $I$ , the result is:

$$\log_e I = \log_e I_0 - \frac{KA}{MLc} t \quad (7)$$

Changing to logarithms to the base 10:

$$t = \frac{2.303MLc}{KA} (\log I_0 - \log I) \quad (8)$$

It is apparent that if values of  $\log I$  are plotted as ordinates with values of  $t$  as abscissas, a straight line will be determined, of slope:

$$P = - \frac{KA}{2.303MLc} \quad (9)$$

Measurement of this slope permits evaluation of  $K$ . It is convenient to use semi-logarithmic paper in making the graph.

### Procedure

Start the water heating in the copper-vessel source, using the electric immersion heater. Turn on the heater only when it is in water. Never place the vessel over a flame.

Have the receiver nearly at room temperature and place the source on the sample to be measured. Connect the constantan (gray) terminals of the source and receiver thermocouples with the constantan wire supplied. Join these in series with the galvanometer and sufficient resistance to give nearly full-scale deflection. After the water in the source has been boiling for several minutes and  $I_0$  has reached a steady maximum, transfer the source and sample to the receiver. The galvanometer deflection will immediately start to decrease. Record the deflection  $I_0$  and time  $t$  every 30 seconds. The time interval may be made 1 or 2 minutes for thick samples, or 15 seconds for thin ones. A dozen or more readings should be made.

To decrease the air film and to insure good thermal contacts, a load of 2 to 4 kg. may be placed on the apparatus during the experiment.

A plot of  $\log I_0$  vs.  $t$  should give a straight line until the copper receiver is warmed appreciably above its surroundings. Measure the slope of the curve, the area  $A$  of the receiver,

and the thickness  $L$  of the specimen. The mass of the receiver will be found stamped on the side. The thermal capacity of copper, at ordinary temperatures, is  $0.093 \text{ cal. gm.}^{-1} \text{ deg. C.}^{-1}$ . Calculate  $K$ , and state its units.

Cool the receiver between runs by placing a copper can filled with ice water on it, but do not wet it. At the conclusion of the experiment rinse and dry the copper vessel and the heater.

#### EXPERIMENT 9

### Thermal Conductivity of a Metal

#### Object

Measurement of the thermal conductivity of copper.

#### Apparatus

Copper bar conductometer. Four thermometers. Boiler with stand and burner. Constant level water tank. Beaker. Pan balance. Electric timer.

#### Discussion

The definition of thermal conductivity  $K$  in

$$Q = \frac{KA t(T_1 - T_2)}{L} \quad (1)$$

suggests a simple method of determining the conductivity of a substance. Using a slab of the material of known cross section  $A$  and length  $L$ , heated on one face, the amount of heat  $Q$  that flows through the opposite face in a known time  $t$  can be measured, as well as the temperatures of the two surfaces  $T_1$  and  $T_2$ . The conductivity can then be determined from Eq. 1.

Actually, precise measurement of the thermal conductivity of materials is difficult and requires many precautions. There are three principle sources of difficulty in conductivity experiments. It is difficult to measure accurately the tem-



peratures of the two faces of the sample. An unknown, large temperature gradient may exist in the thin films of air or liquid that partially insulate the sample. Finally, although a one-dimensional conduction of heat from the hot to the cold face is assumed, there may be considerable loss of heat by conduction and radiation from the edges of the sample.

Figure 164 illustrates the type of copper conductometer used for this experiment. One end of a cylindrical copper bar is enclosed in a steam chamber. The other end is capped by a container through which cool water circulates, thermometers being provided to give its temperature of entry and exit,

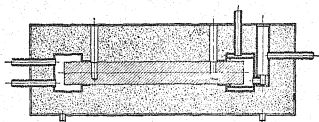


FIG. 164.—Copper conductometer. (Central Scientific Co.)

$T_3$  and  $T_4$  respectively. Two thermometers are inserted into holes drilled in the copper rod and are brought into good thermal contact with the metal by the addition of a few drops of mercury. These read the temperatures  $T_1$  and  $T_2$  at cross section about 10 cm. apart, avoiding the necessity of knowing anything about the fluid layers formed on both ends of the sample. The whole rod is wrapped with a non-conducting material to minimize heat losses. In the steady state if  $M$  grams of water flows through the cooling coil in  $t$  seconds, the heat conducted by the bar per second is  $M(T_4 - T_3)/t$  and this equals  $KA(T_1 - T_2)/L$ , where  $L$  is the distance between the two thermometers  $T_1$  and  $T_2$ . Thus the conductivity  $K$  is determined from:

$$K = \frac{M(T_4 - T_3)L}{tA(T_1 - T_2)} \quad (2)$$

### Procedure

Allow water to flow through the cooling coil, using a constant level water tank to keep the rate of flow constant. Connect the steam jacket to a boiler. When steam is passing through the jacket, adjust the flow of water through the cooling coil, by means of a pinch cock on the supply tube, so that the rise in temperature of the water ( $T_4 - T_3$ ) is about  $10^\circ\text{C}$ . When the readings on the four thermometers have become practically constant, place a weighed beaker below the water outlet, noting the time. Collect water for about 5 minutes, taking thermometer readings every minute. At a noted instant, remove the beaker and determine the mass of water  $M$  collected. Calculate the conductivity of the copper sample from Eq. 2.

## EXPERIMENT 10

### Thermal Conductivity of Gases

#### Object

Determination of the thermal conductivity of several gases by a comparison method.

#### Apparatus

Conductivity cell. Wheatstone bridge. Galvanometer. Milliammeter. Thermostat. Tank samples of several gases such as  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{He}$ ,  $\text{NH}_3$ .

#### Discussion

The electrical energy necessary to heat a platinum wire to a given temperature will depend on the nature of the gas in contact with it, other conditions being equal. The constancy of its temperature may be determined by measuring the resistance of the wire. When a steady state is reached, heat supplied to the wire by electrical energy must equal that

lost to the surrounding thermostat by conduction, convection and radiation. Radiation loss can be minimized by keeping the wire temperature below 400°C. Heat lost from the wire by conduction through its metal supports is a constant which

can be determined for a given apparatus. Then the electrical current necessary to keep the temperature of the wire constant in different gases will be a measure of the thermal conductivity of the gases used.

The heat lost from the wire by conduction

$$Q = \frac{kA(T_2 - T_1)t}{d} + \frac{CA(T_2 - T_1)t}{d} \quad (1)$$

The first term represents heat conducted by the gas. The second term includes heat lost by other means.  $C$  is a constant for a given cell. From the current  $I$  and resistance  $R$  the heat, measured in calories, supplied electrically to the wire may be calculated from

$$Q' = 0.239I^2Rt \quad (2)$$

A steady state is represented by equating  $Q$  and  $Q'$

$$0.239I^2R = \frac{(k + C)A(T_2 - T_1)}{d} \quad (3)$$

which is independent of time. For two gases of conductivities  $k_A$  and  $k_B$  placed successively in the cell

$$k_B = (k_A + C) \frac{I_B^2}{I_A^2} - C \quad (4)$$

If the thermal conductivities are known and the corresponding

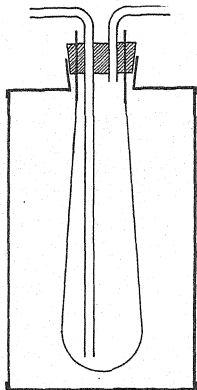


FIG. 165.—Gas conductivity cell. [C. M. Mason and R. M. Doe, *J. Chem. Education*, 14, 182 (1932).]

currents are determined for both gases, the cell constant can be evaluated

$$C = \frac{I_A^2 k_B - I_B^2 k_A}{I_B^2 - I_A^2} \quad (5)$$

The conductivity of any other gas can then be obtained by measuring the corresponding current and solving an equation of the form of Eq. 4.

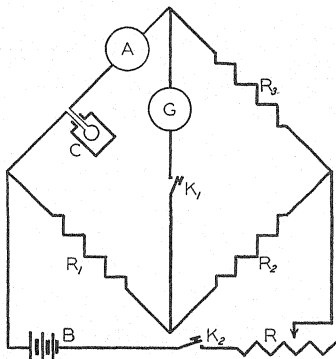


Fig. 166.—Bridge for conductivity measurements.

### Procedure

Place the cell (Fig. 165) in a thermostat. Flow clean, dry air through the cell. Close inlet and outlet tubes and allow the air to come to thermal equilibrium with the thermostat. Make connections to the Wheatstone bridge as in Fig. 166, and set resistors so  $R_1 + R_2 \div 1000$  ohms. This is to prevent burning out the dial resistance box by excessive current. Close switch  $K_2$  and adjust the heavy-duty resistance  $R$  until about 0.15 amp. flows through the cell. Then depress key  $K_1$  and adjust  $R_1$  and  $R_2$  (keeping  $R_1 + R_2 \div 1000 \text{ } \Omega$ )

### Apparatus

Féry total radiation pyrometer with galvanometer temperature indicator. Calibrated thermocouple. Portable potentiometer. Low-range precision potentiometer. Electric furnace with current controller.

### Discussion

Previous study of radiation laws has shown that it is possible to measure the temperature of a body in terms of

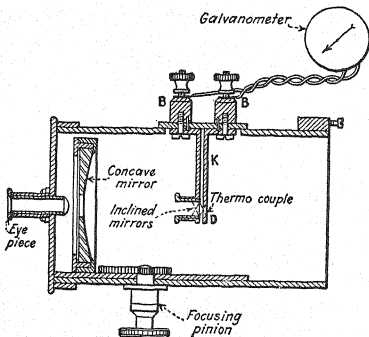


FIG. 167.—Féry radiation pyrometer. (*Bur. Standards Tech. Paper 170.*)

either the energy radiated in a narrow band of wavelengths or the total energy radiated. Instruments employing the first method are called optical pyrometers. They use Wien's law. Instruments for the second method are called total radiation pyrometers. Their operation is described by the Stefan-Boltzmann law.

In the Féry radiation pyrometer (Fig. 167) a concave mirror surfaced with gold, silver or aluminum concentrates radiation from the hot body upon one junction of a small thermocouple. The reference junction of the thermocouple is shielded from

radiation and remains at approximately room temperature. The mirror may be moved by rack and pinion to focus the radiation on the thermocouple. As an aid in securing correct focus, an eyepiece is used in conjunction with two small, plane mirrors placed close to the thermocouple and inclined slightly relative to each other. The effect is to give a divided image of the source. If the pyrometer is not correctly focused, the field of view appears in a divided and displaced image. As the pyrometer mirror is moved into correct focus the divided image moves into alignment.

The galvanometer indicator connected to a radiation pyrometer may be calibrated to read temperatures directly, assuming a blackbody source of radiation. The relation between the deflection of the indicator and the absolute temperature of the source may be predicted on the following assumptions:

(i) The galvanometer deflection  $D$  is proportional to the applied e.m.f.

(ii) The e.m.f.-temperature relation for the thermocouple is linear.

(iii) Newton's law of cooling is applicable to the equilibrium temperature of the thermocouple.

(iv) The net rate of receiving heat is proportional to the difference of the fourth powers of the temperatures of source and surroundings  $T^4 - T_0^4$ , which is the Stefan-Boltzmann law.

These relations may be expressed algebraically,

$$D = a (\text{e.m.f.}) = b(T_2 - T_1) = c(T^4 - T_0^4) \quad (1)$$

or

$$D = AT^4 + B \quad (2)$$

If  $T_0$  is small compared to  $T$ , then  $B$  may be neglected. Eq. 2 can be put in the form,

$$\log D = 4 \log T = \text{constant} \quad (3)$$

Of course the assumptions made above represent only approximately the physical phenomena. The optical system

if a total radiation pyrometer has a transmission (or reflection) coefficient which varies appreciably with the radiation, and hence with the temperature  $T$  of the source. The temperature  $T_0$  of the receiver varies with  $T$ . As a result the e.m.f. is not given by a law in  $T^4$ . Experiment shows that it may be represented as a function of  $T$  by a relation of the form

$$E = m(T^n - T_0^n). \quad (4)$$

where  $n$  is an exponent, constant for a given instrument, whose value varies considerably from the ideal 4.

For measuring high temperatures a diaphragm is placed in front of the pyrometer to suppress part of the incident radiation. The diaphragm is a sector disk so that the central and marginal rays of the objective lens (or mirror) are diaphragmed in the same ratio. If a curve of  $\log T$  vs.  $\log$  e.m.f. is plotted for an instrument thus diaphragmed, it will not generally have the same slope as the corresponding curve obtained for the instrument without the diaphragm. This is explained by the fact that the temperature of the reference junction of the thermocouple, for a given source temperature, is lower than in the absence of a diaphragm.

### Procedure

Put the hot junction of the calibrated thermocouple in a small hole drilled in a block of graphite or nickel and place near the center of the electric furnace. Sight the radiation pyrometer on the furnace opening, using, if necessary, small diaphragms to approximate blackbody conditions in the furnace.

Connect the thermocouple to a portable potentiometer. Use a d.p.d.t. switch to connect the radiation pyrometer in turn to a galvanometer indicator and to a low-range potentiometer.

Plan to take readings at intervals of about  $100^\circ\text{C.}$  over the range available with the furnace used. Prepare a table showing: (i) e.m.f. of standard thermocouple, (ii) tempera-

ture corresponding to that e.m.f., read from tables, (iii) radiation pyrometer e.m.f., (iv) temperature read from pyrometer indicator, (v) temperature calculated from the pyrometer calibration made as described in the next paragraph.

Determine the calibration constants  $m$  and  $n$  from a graph of  $\log E$  vs.  $\log T$ .

For one particular furnace temperature, observe the effect of placing a clear glass plate between the pyrometer and the furnace. Explain.

For a constant furnace temperature, take readings at successively increased distances from the furnace. Explain the effect of distance on the pyrometer readings with the aid of a diagram.

#### EXPERIMENT 13

### Optical Pyrometer

#### Object

Study of the principles of optical pyrometry. (i) Calibration of an optical pyrometer. (ii) Extension of the range of an optical pyrometer. (iii) Determination of the emissivity of a metal.

#### Apparatus

Disappearing-filament type optical pyrometer. Optical-wedge type pyrometer. Broad-filament tungsten lamp with current controller and ammeter. Sector disk with motor. Colored glass filters. Calipers. Electric furnace. Calibrated thermocouple and indicator. Crucible with metal sample.

#### Discussion

Temperature measurement with an optical pyrometer consists in matching monochromatic radiation from the source being measured against that from the filament of a



standard lamp. Comparison is made in some instruments by varying the filament current, in others by varying a wedge filter in the viewing telescope.

The calibrations of optical pyrometers are compared readily by the use of a special accessory lamp. This is the method used in comparing the standards maintained by the various national standardizing laboratories. The comparison lamp has a broad filament. The ribbon may be wedge shape to provide approximately blackbody radiation. Using one pyrometer a curve of current vs. temperature is prepared for the comparison lamp. The lamp with this curve is then used to check the calibration of a second pyrometer when sighted upon it.

The range of an optical pyrometer is extended by decreasing the radiation from the source by a known factor. If a filter of thickness  $t$  having absorption coefficient  $k$  is placed before the pyrometer its scale reading  $T_a$  is related to the true temperature of a blackbody source by,

$$\frac{1}{T} - \frac{1}{T_a} = -\frac{k\lambda t}{c_2} = \text{constant} \quad (1)$$

Alternatively a rotating sector disk may be used to reduce the incident radiation. If the ratio of open to closed sectors is  $A$  the relation between true and indicated temperatures becomes

$$\frac{c_2}{\lambda T} \left\{ \frac{1}{T} - \frac{1}{T_a} \right\} = \log_e A \quad (2)$$

If an optical pyrometer calibrated for blackbody conditions is used for measurements on a surface of emissivity  $e_\lambda$  the observed temperature is related to the true temperature by

$$\log_e e_\lambda = \left\{ \frac{1}{T} - \frac{1}{T_a} \right\} \quad (3)$$

### Procedure

Compare the calibrations of two optical pyrometers, with the aid of the ribbon filament lamp. Show the agreement or discrepancy in a graph.

From paper or thin sheet aluminum prepare a disk similar to Fig. 168. The total angular opening should be about  $30^\circ$ . Sight one of the pyrometers through the open sector of the stationary disk and read the temperature of the incandescent filament of the comparison lamp. Repeat the reading when the disk is spinning, keeping the current in the comparison lamp constant. Compare the second pyrometer reading with that calculated from Eq. 2.

Determine the emissivity of a molten metal by obtaining its true temperature from a calibrated thermocouple and reading its apparent temperature on an optical pyrometer. The emissivity is given by Eq. 3. Compare results obtained when the optical pyrometer is sighted on the bright surface of the metal and then on the surface covered with oxide or with powdered graphite. If all measurements are made at the solidifying temperature of the metal they may be readily reproduced and checked. If a two-color optical pyrometer is available, compare the temperature obtained from its two readings on a bright surface with that indicated by the thermocouple.

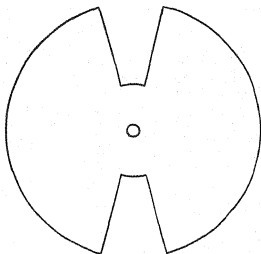


FIG. 168.—Sectored disk.

#### EXPERIMENT 14

### The Radiation Constant, Calorimetric Method<sup>1</sup>

#### Object

Determination of the value of the constant  $\sigma$  in the Stefan-Boltzmann radiation law.

<sup>1</sup> A. D. Denning, *Phil. Mag.* (6) 10, 210 (1905).

### Apparatus

Copper can with hemispherical bottom. Silver disk. Two copper-constantan thermocouples. Potentiometer or galvanometer. Timer. Calipers. Dewar flask. Boiler. Bunsen burner. Camphor.

### Discussion

An approximate value for the constant  $\sigma$  of the Stefan-Boltzmann radiation law can be obtained by a calorimetric

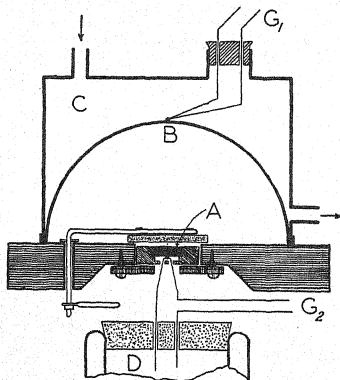


FIG. 169.—Radiation constant apparatus.

method using simple apparatus. A hemispherical radiator  $B$  (Fig. 169) is heated to the steam temperature, then placed over a silver disk  $A$  of known area  $A$ , mass  $M$  and thermal capacity  $c$ . Both the disk and the concave surface of the hemisphere are blackened. From the initial rate of rise of temperature  $dT/dt$  observed for the disk,  $\sigma$  may be calculated from Eq. 1.

Let  $R_1$  be the radiation absorbed by the disk per second per unit area, and  $R$  be the rate at which radiation is emitted per unit area. The energy gained by the disk per second is then  $(R_1 - R)A$ , where  $A$  is the exposed area of the disk.

From the general equation of calorimetry and the Stefan-Boltzmann law:

$$Mc \frac{dT}{dt} = \frac{R_1 - R}{J} A = \frac{\sigma A}{J} (T_1^4 - T^4)$$

and

$$\sigma = \frac{JMc}{A(T_1^4 - T^4)} \frac{dT}{dt} \quad (1)$$

where  $T_1$  is the temperature of the copper hemisphere,  $T$  the temperature of the silver disk,  $t$  the time in seconds and  $J$  the mechanical equivalent of heat.

### Procedure

After weighing and measuring the silver disk, blacken it and the hemisphere over burning camphor. Connect a boiler to steam chamber  $C$  and pass steam through to heat hemisphere  $B$ . The temperature of the hemisphere may be taken as that of the steam (determined from a barometer reading and steam tables) or it may be measured by a thermocouple soldered at  $B$  and connected to a galvanometer at  $G_1$ .

One junction of a thermocouple is soldered to the silver disk, the other junction placed in a Dewar of melting ice and the leads connected to a galvanometer at  $G_2$ . When the hemisphere has reached a steady temperature, place it over the disk. At a noted time, remove the fiber insulation from the surface of the disk and commence a series of temperature (or e.m.f.) readings at definite time intervals for about 15 minutes.

Plot a temperature-time (or e.m.f.-time) graph. Evaluate  $dT/dt$  from a tangent. Using the appropriate value of  $T$ , calculate  $\sigma$ .

## EXPERIMENT 15

## Radiation Constant, Equilibrium Method

## Object

Determination of the constant in the Stefan-Boltzmann radiation law.

## Apparatus

Copper sphere enclosing an electric heater. Voltmeter. Ammeter. Variable resistor. Thermocouples and galvanometer. Vacuum-jacketed cylindrical vessel. Mechanical and mercury diffusion vacuum pumps (optional). Calipers.

## Discussion

As an alternative to the method of Exp. 14, the radiation constant can be determined accurately from the electric power supplied to a copper sphere to maintain its temperature at a certain value when it is losing heat by radiation only.

A hollow, blackened copper sphere is provided with an electric heater and a thermocouple and is suspended inside a closed Dewar flask. Power is supplied at a constant rate until the thermocouple indicates an equilibrium temperature  $T$ . The sphere is then radiating as fast as it receives heat. Hence

$$\frac{EI}{J} = 4\pi r^2 \sigma (T^4 - T_w^4) \quad \text{or} \quad \sigma = \frac{EI}{4\pi J r^2 (T^4 - T_w^4)} \quad (1)$$

The power  $EI$  is calculated from voltmeter and ammeter readings.  $T_w$  is the temperature of the walls surrounding the sphere.  $J$  is the mechanical equivalent of heat.

If vacuum pumps are available, the space between the sphere and the vacuum-jacketed container may also be evacuated. This eliminates heat loss by convection and improves the accuracy of the experiment.

## EXPERIMENT 16

## Surface Temperature Measurement

**Object**

Comparison of various methods of measuring surface temperatures in the range 25°C. to 250°C.

**Apparatus**

Electrically-heated test plates. Current controller. Voltmeter. Ammeter. Dewar flask. Two mercury thermometers calibrated for total and partial immersion respectively. Several types of commercial surface thermocouples. Potentiometer. Thermocolors.

**Discussion**

An experimental comparison of the precision obtainable with various methods of measuring surface temperatures requires a surface whose temperature can be controlled and measured accurately. This is provided by the electric heater illustrated in Fig. 170. A resistance wire  $R$  is wound in a flat spiral, insulated with asbestos paper  $A$  and clamped between two iron plates  $P$  measuring approximately 20 cm. square and 0.5 cm. thick. Temperatures are indicated by iron-constantan thermocouples, the iron plate serving as one element of the couple. A leg extending from one plate, to the bottom of which a constantan wire is welded, serves as the reference junction which may be immersed in an ice bath.

For a given heater current, the heat loss from the plates may be calculated from

$$\frac{Q}{At} = \frac{EI}{4.18 \times 2A} \text{ cal./cm.}^2 \text{ sec.} \quad (1)$$

Here  $E$  is the voltage and  $I$  the current in amperes supplied

to the heater, and  $A$  is the surface of one face in  $\text{cm.}^2$  Using thermocouple leads 1 and 3 the temperature  $T_1$  of the inner face of the iron plate may be measured accurately. The

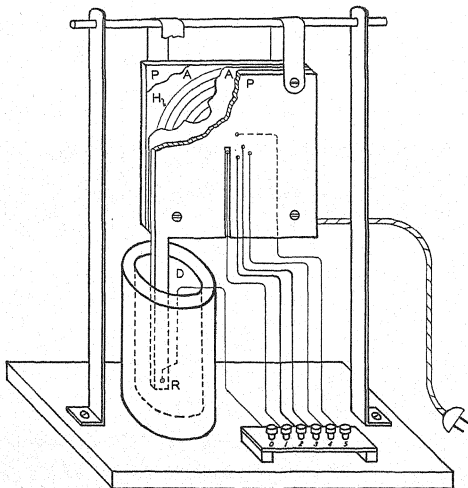


FIG. 170.—Surface temperature test plate.

temperature of the outer face is readily calculated if the thickness  $l$  and conductivity  $k$  of the iron plate are known,

$$T_1 - T_2 = \frac{Ql}{kAt} = \frac{EIl}{4.18 \times 2Ak} \quad (2)$$

The calculated difference between the temperatures of the inner and outer faces of the plate will be found to be negligibly small. Hence a thermometer or thermocouple placed in contact with the outer face of the plate might be

expected to indicate a temperature equal to  $T_1$ . Actually the temperature indicated will be somewhat lower. The chief sources of this error are: (i) the presence of a gas film causing a temperature drop between plate and instrument, (ii) heat conduction along the instrument, especially if it has a large cross section and (iii) radiation from the instrument, especially if it has considerable exposed area. The design of instruments for measuring surface temperatures accurately is largely concerned with the reduction of these sources of uncertainty.

### Procedure

Compare the temperature readings of total and partial immersion mercury thermometers held in contact with the plate in a manner suited to their immersion requirements. Try both upright and horizontal positions for the thermometers. Loss of heat from the thermometer bulbs may be decreased by a thin covering of paste made from asbestos and oil.

Observe the temperature indicated by several types of commercial surface thermocouples in contact with the plate. Or, alternatively, construct a thermocouple of No. 28 gauge wires and one of No. 20 gauge wires, fasten to the surface of the plate with asbestos paste and compare the temperatures indicated.

A constantan wire is spot welded to the iron plate. The wire leaves this junction in a shallow channel cut in the plate, making good thermal contact with the plate but insulated electrically from it except at the weld. Compare the temperature indicated by this thermocouple (leads 2 and 3, Fig. 170) with those indicated by the other instruments.

Thermocolors are temperature-sensitive paints which change color, reversibly or irreversibly, at one or more definite temperatures. Spot several paint samples on the iron plate and check the temperature data supplied for them by the manufacturer.



In reporting the results of this experiment, obtained at different plate temperatures, use graphical comparisons wherever possible.

#### EXPERIMENT 17

## Measurement of Flame Temperature

### Object

Measurement of the temperature of a luminous flame by a spectroscopic line-reversal method. Comparison of results with those of other available methods.

### Apparatus

Burner with sodium-coloring attachment. Spectroscope. Broad-filament tungsten lamp. Optical pyrometer. Thermocouples. Potentiometer.

### Discussion

Strictly speaking, measurement of any thermodynamic property of a system may be made, and a definite meaning attached to the result, only when the system is in complete equilibrium. Obviously gases burning turbulently in an open flame or in an engine are not in complete equilibrium.

If anything approaching instantaneous thermal equilibrium exists, it is important to have a method of measuring temperatures the response of which will be instantaneous. To obtain instantaneous values of effective temperature the thermometric substance must be distributed throughout the region whose temperature is desired, and must have a heat capacity negligible as compared with that of the substances in combustion. These conditions can be satisfied by introducing a very small quantity of a thermometric substance which is easily vaporized. The temperature of this substance can then be found by comparing its brightness at any given wavelength with that of a continuous radiation

whose brightness temperature at that wavelength is known. The amount of vapor present must be sufficient to reflect and absorb light according to Kirchhoff's law. This condition can be attained with extremely small quantities of vapor if comparison is made at a wavelength corresponding to some resonance radiation of the vapor. Under these circumstances investigation has shown that the thermometric substance has a negligible effect on the flame temperature.

The method of temperature measurement just outlined is known as the line reversal method, and has been used

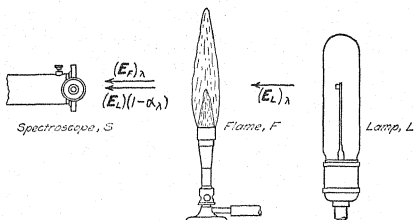


FIG. 171.—Diagram of line reversal apparatus. (A. E. Hershey and R. F. Paton, *Bulletin No. 262 Engineering Experiment Station, University of Illinois.*)

extensively in measuring the temperature of a wide variety of flames.

In Fig. 171,  $F$  represents a bunsen flame into which a metallic vapor such as sodium is introduced. The vapor must be that of an element whose resonance radiation is in a wavelength region which can be easily observed. Radiation from the tungsten ribbon filament lamp at  $L$  passes through the flame to the slit of the spectroscope at  $S$ . The flame is practically transparent to radiation in the visible region except at  $\lambda$ , the wavelength of the resonance radiation of the metallic vapor in the flame.

Let  $(E_L)_\lambda$  and  $(E_F)_\lambda$  be the radiant energy at wavelength  $\lambda$  from the lamp filament and the flame, respectively, and let  $\alpha_\lambda$  be the absorptivity of the flame at the same wave-

length. The energy incident upon the slit of the spectroscope at this wavelength is  $(E_F)_\lambda + (1 - \alpha_\lambda)(E_L)_\lambda$ , assuming that reflection at the flame surface is negligible. If  $(E_F)_\lambda > \alpha_\lambda(E_L)_\lambda$ , a bright line will be observed, crossing the continuous spectrum of the filament at  $\lambda$ . If, however,  $(E_F)_\lambda < \alpha_\lambda(E_L)_\lambda$  a dark or reversed line will appear at this wavelength. For the particular case when  $(E_F)_\lambda = \alpha_\lambda(E_L)_\lambda$  neither the bright nor the reversed line will be seen, and the flame will be emitting as much energy of wavelength  $\lambda$  as it is absorbing. If the flame satisfies Kirchhoff's law, then  $(E_F)_\lambda / \alpha_\lambda = E_\lambda$ , where  $E_\lambda$  is the radiant energy of a perfect radiator at wavelength  $\lambda$ , the temperature of this radiator being the same as that of the vapor in the flame. Therefore  $(E_L)_\lambda = E_\lambda$ , and from Wien's law the brightness temperature of the lamp filament  $T_L$  is equal to the true temperature  $T$  of the vapor in the flame.

The brightness temperature of the lamp filament can be measured with an optical pyrometer so that the true temperature of the flame can be readily determined. However, when the effective wavelength of the pyrometer screen is not the same as that of the resonance radiation of the vapor in the flame, it is necessary to make a slight correction for the variation in emissivity of the lamp filament between these two wavelengths. If  $\epsilon_\lambda$  is the monochromatic emissivity of the filament at wavelength  $\lambda$  then

$$\frac{1}{T} - \frac{1}{T_L} = \frac{\lambda}{c_2} \ln \epsilon_\lambda$$

Evaluating this equation for the two wavelengths, and eliminating  $T$  we have,

$$\frac{1}{(T_L)_{\lambda_2}} = \frac{\lambda_1}{c_2} \ln \epsilon_{\lambda_1} - \frac{\lambda_2}{c_2} \ln \epsilon_{\lambda_2} + \frac{1}{(T_L)_{\lambda_1}}$$

where  $\lambda_1$  is the effective wavelength of the pyrometer screen and  $\lambda_2$  the wavelength of the radiation from the vapor. The pyrometer measurement gives the value of  $(T_L)_{\lambda_1}$ , the con-

stant  $c_2$  is the same for all temperatures, the emissivity for a tungsten filament is known over a wide range of wavelengths and temperatures, and hence the value of  $(T_L)_{\lambda_2}$  which is equal to the true flame temperature  $T$  can be calculated.

### Procedure

Using apparatus arranged as in Fig. 171, determine the temperature of a laboratory flame by the line reversal method. Make the appropriate correction for the different emissivities of the filament at the effective wavelength of the pyrometer screen ( $0.65\mu$ ) and the wavelength of the resonance radiation ( $5893 \text{ \AA}$ . for sodium vapor).

Observe the temperature of the flame with an optical pyrometer and an auxiliary source, following the method illustrated by Fig. 129.

Finally, estimate the temperature of the flame by placing in it bare thermocouples of successively smaller diameter wires and extrapolating the indicated temperature to zero wire diameter.

Account for the discrepancies in the results of these three methods of flame temperature measurement. Discuss the reliability of flame temperature measurements.

## EXPERIMENT 18

### Pyrometric Cones

#### Object

Investigation of the response of pyrometric cones to heat treatment.

#### Apparatus

Furnace. Thermocouple pyrometer. Optical pyrometer. Pyrometric cones.

### Procedure

Outline an experimental procedure for investigating the following characteristics of a series of pyrometric cones:

1. Accuracy of the softening temperature calibration when heated at the specified rate.
2. Uniformity of similar cones.
3. Effect of rapid and slow heating rates on the softening temperature.
4. Response of cones to oxidizing and reducing atmospheres.

After the outline of the proposed procedure has been approved by the instructor, carry out the experiment. Use graphs in your report, where possible, to indicate the significance of the observations.

## EXPERIMENT 19

### Simple Fuel Calorimeter

#### Object

To obtain the heating value of coal and fuel oil samples.

#### Apparatus

Cussons fuel calorimeter. Oxygen cylinder with reducing valve. Woulffs bottle. Thermometer. Balance. Samples of coal and fuel oil. Sulphur.

#### Discussion

Figure 172 represents an elementary form of fuel calorimeter. It consists of a copper tube around which is wound a spiral of small-bore copper tubing, the whole being immersed horizontally in a water bath. The bath is surrounded and supported on heat insulating material.

Combustion is carried out in the horizontal tube. The fuel is measured into a porcelain, quartz or nickel boat,

which is introduced into the tube at the open end into which a copper plug is afterward inserted. The products of combustion are expelled through small holes in the coil and bubble through the water. A continuous stream of oxygen at low pressure is introduced through the inlet tube to secure steady and complete burning. With the exception of the combustion boat the whole apparatus is made of copper, so that the water equivalent may be determined readily.

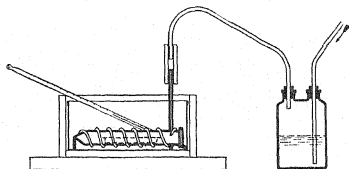


FIG. 172.—Simple fuel calorimeter. (*G. Cussons, Ltd.*)

From the rise in temperature  $t_1 - t_2$  produced in the calorimeter by the combustion of  $M$  grams of fuel the heat of combustion may be calculated:

$$H = \frac{(W + B)(t_1 - t_2)}{M} c_w \quad (1)$$

$W$  is the weight of water in the bath,  $B$  is the water equivalent of the apparatus and  $c_w$  is the thermal capacity of water.

### Procedure

Spread the fuel sample evenly along the combustion boat. If a liquid is used, introduce a little kaolin to absorb it. Insert the boat for most of its length in the tube. Place a bit of sulphur on the fuel and ignite it. Immediately push the boat to the center of the tube, cap the tube and immerse it. Read the thermometer. Adjust the oxygen supply to give a slow, steady bubbling of the exhaust gases. Take temperature readings at intervals of about one minute.

From the initial and maximum temperatures observed, calculate the heat of combustion for the sample.

## EXPERIMENT 20

# Oxygen Bomb Calorimeter

### Object

Determination of the heat of combustion of a fuel with an oxygen bomb calorimeter.

### Apparatus

Parr oxygen bomb calorimeter with accessories. Thermometer. Tank of compressed oxygen. Electric timer. Analytical balance. Pan scales. Graduate. Three beakers. Burette. Wash bottle. Methyl orange. Sodium carbonate. Benzoic acid. Coal sample.

### Discussion

One of the most important tests of material used primarily for fuel is the determination of the amount of heat generated by the complete combustion of unit mass of the material. This quantity, called the heat of combustion, is commonly expressed in calories per gram, large Calories per kilogram or B.t.u. per pound.

Instruments employed for this type of measurement are known as calorimeters. They are of two distinct types, depending upon whether they are designed for testing solid and liquid samples or for testing gases. The calorimeter used in this experiment is of the first type. Gas calorimetry is discussed in the next experiment. In all commonly used calorimeters a known weight of the sample is burned completely in an apparatus which permits the heat developed by the combustion to be absorbed by a definite mass of water. From the rise in temperature of the water it is possible to calculate the number of heat units liberated. In calorimeters

for solid and liquid samples, complete combustion is insured by use of oxygen gas under pressure or the use of sodium peroxide as the oxidizing agent.

An oxygen bomb calorimeter consists of three essential parts: (i) the bomb or container in which the sample is burned, (ii) the calorimeter vessel or bucket, containing a

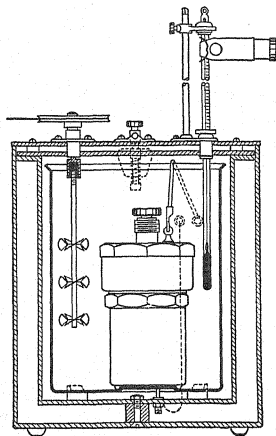


FIG. 173.—Section of oxygen bomb calorimeter. (Parr Instrument Co.)

measured quantity of water in which the bomb, stirring device and thermometer are immersed, and (iii) the jacket, for minimizing heat transfer between the calorimeter and its surroundings. These parts are illustrated in Fig. 173.

The bomb and its mechanically-sealed cover must withstand normal working pressures of 100 to 150 atmospheres and maximum pressures up to about 600 atmospheres (8820 lbs./in.<sup>2</sup>). Nitrogen of the air and any sulphur present in the sample burned are converted into acids which, with



the excess oxygen at high temperature, form a corrosive atmosphere which will etch ordinary metals. In early forms of bombs a lining of platinum, gold, enamel or nickel was used to retard corrosion. In the Parr instrument the bomb is made of a proprietary alloy, illium.

The accuracy of calorimetric measurements is largely dependent upon the accuracy with which calorimeter temperatures are read. Either a Beckmann or a solid-stem mercurial thermometer is commonly used. The small range of a Beckmann thermometer ( $5^{\circ}$  Centigrade), together with the need for applying several corrections for each test, usually offsets the advantage of finer graduations in that type of thermometer. For general calorimetric use a solid-stem thermometer is preferable. This may be about 24 inches long and cover the range from  $65^{\circ}\text{F.}$  to  $90^{\circ}\text{F.}$  in units of  $0.05^{\circ}\text{F.}$  When readings are taken with a lens temperatures can be estimated to the nearest  $0.005^{\circ}\text{F.}$  Each thermometer is generally supplied with an individual certificate showing in chart or tabular form the corrections to be applied to its scale readings.

When a calorimeter is at a higher temperature than its surroundings it loses heat, and when at a lower temperature it gains heat from the surroundings. In making precise calorimetric measurements it is essential to minimize this source of error. In addition to insulating the calorimeter, there are several methods of diminishing further the error due to radiation.

In Rumford's method a preliminary trial is made to ascertain the approximate rise in temperature. The calorimeter is then cooled half this number of degrees below room temperature,  $T_r$ , before the next experiment. Then the amount of heat gained by the calorimeter during the time its temperature is below  $T_r$  partially compensates for the amount lost by it while its temperature is above  $T_r$ . This compensation is only approximate, owing to the fact that the rate of increase of temperature with time,  $dT/dt$ , diminishes

rapidly as the calorimeter and its surroundings approach thermal equilibrium. Hence the calorimeter remains a longer time above the temperature of its surroundings than below, and receives a net heat gain.

Rowland's method (Ferry's modification) of making a radiation correction is illustrated by Fig. 174. The curve *ABDE* represents the successive temperatures of a calorimeter which has the same temperature as its surroundings at *C*. The corrected initial and final temperatures, *h* and *f*, are obtained by producing *AB* and *ED* to intersect the vertical through *C*. Then the temperature change, corrected for radiation, is given by *hf*. It will be noted that this graphical method is based upon Newton's law of cooling, and hence its validity is limited to small differences in temperature,

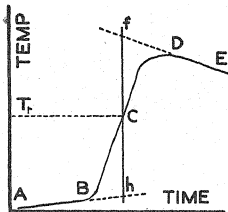


FIG. 174.—Rowland's method.

of the order of 20°C. This is not a serious limitation in most calorimetric work. Rowland's method may be employed even when  $T_r$  does not lie between the initial and final calorimeter temperatures.

Dickinson's "60%" method, to be used in this experiment, is similar to that of Rowland except that the intersection *m* (Fig. 175) of the vertical and the heating curve is taken at a time  $t_m$  when the calorimeter has reached 0.6 of its final temperature. This may be justified as follows. It should be possible to find a time  $t_m$  such that the radiation correction *A* may be written:

$$A = \alpha \int_{t_1}^{t_2} (T - T_0) dt = r_1(t_m - t_1) = r_2(t_2 - t_m) \quad (1)$$

where  $r_1$  and  $r_2$  are the rates of cooling at times  $t_1$  and  $t_2$ , respectively, corresponding to the time of firing the charge and the time the final temperature is attained.  $\alpha$  is the cooling

constant for the calorimeter. Geometry suggests that the condition expressed in Eq. 1 is satisfied if  $t_m$  is so chosen that the shaded areas between the curve and the lines  $T_1$  and  $T_2$  are equal on either side of it. If the curve is plotted it is a simple matter to locate  $t_m$ . Experience has shown, however, that the position of  $t_m$  with respect to  $t_1$  and  $t_2$  is remarkably constant for a combustion calorimeter used with sufficient stirring. The line  $t_m$  crosses the temperature-time curve

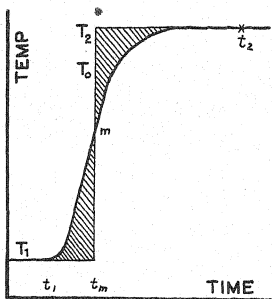


FIG. 175.—Dickinson's "60%" method.

always at nearly the same relative position. This experimental fact suggests the following calculation.

If heat generated in the bomb were all distributed instantly to the walls of the bomb, giving it a temperature  $T_b$ , the rise in temperature of the water would follow closely an exponential expression obtained from integrating Newton's law,  $dT/dt = k(T - T_b)$ , i.e.:

$$T = T_b(1 - e^{-kt}) \quad (2)$$

To satisfy the condition of equal areas given above:

$$T_b \int_0^{t_m} [1 - e^{-kt}] dt = \int_{t_m}^{\infty} [T_b - T_b(1 - e^{-kt})] dt$$

Integrating and simplifying, this becomes:

$$t_m = \frac{1}{k}$$

If this is substituted in Eq. 2 one obtains the value  $T_m$  corresponding to  $t_m$ :

$$T_m = T_b(1 - e^{-\frac{k}{k}}) = 0.63T_b \quad (3)$$

Thus if the time is observed when the temperature rise reaches 0.63 of its final value, this time may be used as  $t_m$ .

Dickinson remarks that a large number of observations for which curves were plotted gave 0.57 to 0.62, always slightly less than that for the exponential curve. This may be attributed to the fact that the temperature rise does not begin instantaneously as assumed above.

### Sample Data and Calculations

	Time, min.	Temperature, °F.
	0	74.825
	1	74.830
	2	74.835
	3	74.840
	4	74.845
(a)	5	74.850
	5.25	74.920
	5.50	75.280
	5.75	77.100
	6.0	78.530
(b)	6.191	79.506
	6.25	79.810
	6.50	80.610
	6.75	81.220
	7.75	82.290
	8.75	82.510
	9.75	82.605

	Time, min.	Temperature, °F.
(c)	10.75	82.610
	11.75	82.605
	12.75	82.600
	13.75	82.590
	14.75	82.585
	15.75	82.565

**Thermometer corrections**

Initial reading: 74.850    Final reading: 82.610

Scale correction: .001    Scale correction: .000

Initial Temperature: 74.851    Final temperature: 82.610

Observed temperature rise: 7.759°F.

0.6 of rise in temperature: 4.655

Temperature when 0.6 rise is attained: 79.507

Time when 0.6 rise is attained: 6.191 min.

$(79.810 - 78.530) / 15 = 0.0853^\circ\text{F.}/\text{sec.}$

$(79.507 - 78.530) / 0.0853 = 11.45 \text{ sec.} = 0.191 \text{ min.}$

**Radiation correction for initial period**

Duration of preliminary period  $(b - a)$ :  $6.191 - 5 = 1.191 \text{ min.}$

Rate of rise:  $r_1 = (74.850 - 74.825) / 5 = 0.005^\circ\text{F.}/\text{min.}$

Correction to initial temperature:  $r_1(b - a) = (.005)(1.191) = 0.0059^\circ\text{F.}$

Corrected initial temperature: 74.856°F.

**Radiation correction for final period**

Duration of final period  $(c - b)$ :  $10.75 - 6.191 = 4.559 \text{ min.}$

Rate of fall:  $r_2 = (82.610 - 82.565) / 5 = .009^\circ\text{F.}/\text{min.}$

Correction to final temperature:  $r_2(c - b) = (4.559)(.009) = 0.041^\circ\text{F.}$

Corrected final temperature: 82.651°F.

Net corrected temperature rise:  $7.795^{\circ}\text{F.} = 4.331^{\circ}\text{C.}$

Total water equivalent for calorimeter: 2511 gm.

Total heat liberated:  $(2511)(4.331) = 10,875 \text{ cal.}$

Corrections: fuse wire:  $(10 - 1)(2.8) = 25.2 \text{ cal.}$

volume  $\text{Na}_2\text{CO}_3$  used in titrating:

32 ml.

32.

sulphur:  $(1.4447)(0.015)(1321) =$

28.7

total correction:

85.9 cal.

Net heating value of coal sample:

$(10,875 - 86) / 1.4447 =$

7,468 cal. /gm.

$= 13,442 \text{ B.t.u. /lb.}$

For a detailed discussion of the method of sampling coal the student is referred to the recommendation of the American Society for Testing Materials, published in the A.S.T.M. Volume of Standards for 1933. Assuming that a coal sample has been obtained and pulverized, the procedure for determining its heat of combustion may be given conveniently in outline form.

### Procedure

1. Weigh accurately about 1 gm. of coal in the fuel capsule.

2. Attach the fuse wire (10 cm.) and set the fuel capsule in place in the loop electrode.

3. Wet the rim of the bomb cylinder with moist finger tips, set the cover in place, taking care not to upset the sample. Place the bomb in the bench socket and tighten the cap with a wrench. Fill the bomb with oxygen, slowly, to a gauge pressure of 20 atm. Screw the protective nut over the bomb check valve.

4. Add 2000 gm. of water to the calorimeter bucket. The temperature of the water is to be adjusted so that the final temperature, after combustion, will not be more than  $1^{\circ}\text{F.}$  above room temperature. This means that the initial

temperature usually should be approximately  $3^{\circ}\text{F}$ . below room temperature.

5. Place the bucket of water in the calorimeter, set the bomb in the bucket, attach the clip terminal of the firing circuit to the bomb, close the cover, insert the thermometer, attach the pulley and drive belt and start the stirring motor.

6. Allow the stirrer to run for at least two minutes, then record thermometer readings at one-minute intervals for a period of five minutes.

7. On the fifth minute, fire the charge by closing the ignition switch. Open the switch immediately after the pilot lamp ceases to glow. (Why?)

8. Record the thermometer readings at 15-second intervals for two minutes after firing the charge. Then continue readings at one-minute intervals until five minutes after a maximum temperature is reached.

9. Dismantle the calorimeter, release the residual pressure and open the bomb.

10. Remove carefully the pieces of the 10 cm. fuse wire which remain, and measure the combined length of the pieces.

11. Rinse all inner surfaces of the bomb with distilled water and collect the washings in a clean beaker. Titrate the washings with a standard sodium carbonate solution using methyl orange indicator, to determine the amount of acid formed.

An outline of the calculations required to give the heat of combustion from these data is given in the following paragraphs.

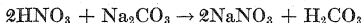
1. Apply the proper scale and radiation corrections to the initial and final temperatures.

2. Determine the total heat liberated by multiplying the net temperature rise by the total water equivalent of the calorimeter.

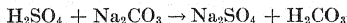
3. Subtract from the total thermal units a correction of 2.8 cal. for each cm. of fuse wire burned.

4. Subtract the correction for acids formed, based upon the titration. If a solution containing 3.658 gm. of  $\text{Na}_2\text{CO}_3$  per liter is used, the correction will be 1 cal. for each ml. of solution used in titrating.

If the sample were free of sulphur, the correction here considered would be for nitrogen, each gram of which when oxidized in the bomb and absorbed in water to form  $\text{HNO}_3$ , liberates 1035 cal. The amount of  $\text{HNO}_3$  formed is measured by titration with  $\text{Na}_2\text{CO}_3$  according to the reaction:



Most fuels contain sulphur which is oxidized and converted to  $\text{H}_2\text{SO}_4$  in the bomb. When S in a fuel burns to  $\text{SO}_2$  in ordinary combustion it liberates 2162 cal. per gm. of S. But when, in the oxygen bomb, it burns to  $\text{SO}_3$  and is absorbed in water to form  $\text{H}_2\text{SO}_4$  it liberates 4389 cal. per gm. Therefore, the combustion of S in the bomb liberates  $4389 - 2162 = 2227$  cal. per gm. more than is liberated in normal burning, and correction must be made for that amount. When  $\text{H}_2\text{SO}_4$  is present in the bomb washings the following reaction occurs during titration, in addition to the one above:



Rather than attempt to separate the  $\text{HNO}_3$  and the  $\text{H}_2\text{SO}_4$  to determine the amount of each, it is convenient to compute the acid correction based on the assumption that only  $\text{HNO}_3$  is present. However, the heat liberated by the formation of  $\text{H}_2\text{SO}_4$  is greater than that liberated when an equivalent amount of  $\text{HNO}_3$  is formed. It is necessary to apply an extra correction for the heat generated by the  $\text{H}_2\text{SO}_4$  in addition to that which is accounted for in the titration (i.e., 906 cal. per gm. of S). This additional correction is 2227 —



906 = 1321 cal. per gm. of S. Subtract this correction together with that described in the first paragraph of (4).

5. Having subtracted the foregoing corrections for fuse, acids and sulphur from the total thermal units, divide the remainder by the weight of the coal sample to determine its heat of combustion.

A convenient form for data and calculations is given on page 366. When many determinations are to be made, calculations may be facilitated by the use of nomographs.<sup>1</sup>

The use of a calorimeter to determine the heat of combustion of a fuel requires knowledge of the total heat capacity of the calorimeter. This may be expressed conveniently in terms of the "water equivalent" of the calorimeter, which includes that of the container, the water, the bomb and its contents, and parts of the thermometer, stirring device and supports for the container. Rather than calculate or measure these individually, it is convenient to determine the total water equivalent of the calorimeter from the combustion of a known amount of a standard material whose heat of combustion is accurately known.

Three materials are commonly used for standard combustion samples.<sup>2</sup> In order of their suitability they are:

1. Benzoic acid. Heat of combustion is about 6320 cal. per gm. This material is not very hygroscopic, burns easily and completely and may be compressed readily into pellets for ease in handling.

2. Naphthalene. Heat of combustion is about 9614 cal per gm. This material is rather volatile but not hygroscopic. Some care is necessary to avoid errors due to sublimation.

3. Sucrose or cane sugar. Heat of combustion is about 3949 cal. per gm. This material is neither volatile nor strongly hygroscopic, but it is difficult to ignite and occasionally does not burn completely.

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<sup>1</sup> Parr Instrument Company, *Parr Oxygen Bomb Calorimeters* . . . , Moline, Ill., 1938.

<sup>2</sup> Obtainable from the National Bureau of Standards.

## EXPERIMENT 21

## Gas Calorimeter

**Object**

Measurement of the heating value of gas in a water-flow-type gas calorimeter.

**Apparatus**

Sargent-type calorimeter. Gas meter. Pressure regulator. Pan balance, with weights. Two beakers. Four thermometers. Gas burner. Psychrometer. Gas Calorimeter Tables.<sup>1</sup>

**Discussion**

The total heating value of a gas refers to the number of heat units generated by the combustion of a unit volume of the gas. The volume is usually reduced to standard conditions: the volume the gas would occupy when saturated with water vapor at 60°F. and under a pressure equivalent to that of 30 inches of mercury at 32°F. Recently there has been a tendency to express the heating value under conditions actually existing at the time of measurement of the gas for use.

The net heating value of the gas is defined as the total heating value less the heat of vaporization, at the initial temperature of the gas and air, of the water formed in the combustion of the gas.

Gas is passed through a meter (Fig. 176) and pressure regulator and is burned in the calorimeter (Fig. 177). The temperatures of the gas as it enters the burner and the products of combustion as they leave the calorimeter are read on thermometers. A stream of water flows through the calorimeter jacket, its rate being controlled by a valve

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<sup>1</sup> Nat. Bur. Standards Circular C417.

and a constant-level reservoir, and is collected in a measuring vessel. Thermometers are placed to read the temperature of the water as it enters and leaves the calorimeter. Water vapor formed by combustion of the gas condenses and is collected in a separate beaker.

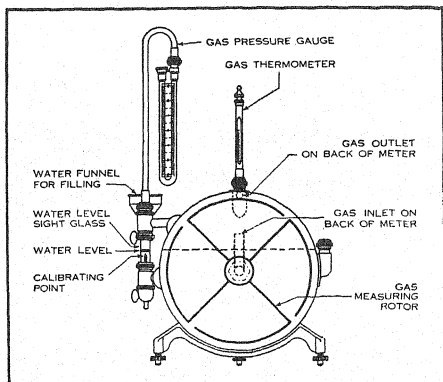


FIG. 176.—Wet test gas meter. (*Precision Scientific Instrument Co.*)

The heating value of the gas  $H$  is given by the equation

$$H = \frac{M_w c_w (t - t') - M_s L_v - M_s c_w (t_s - t_c)}{V} \quad (1)$$

$V$  is the volume (reduced to normal standard conditions) of gas burned in a given time.  $M_w$  is the weight of water passing through the calorimeter in that time.  $t'$  and  $t$  are temperatures of the water entering and leaving the calorimeter.  $M_s$  is the weight of steam condensed;  $t_s$  and  $t_c$  are the temperatures at which it condenses and that at which the condensate leaves the calorimeter.  $c_w$  is the mean thermal capacity of water, and  $L_v$  its latent heat of vaporization.

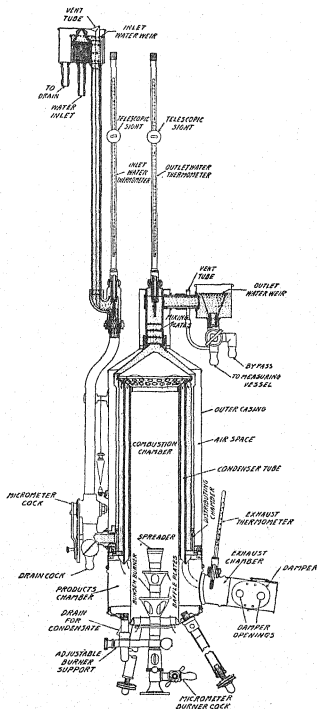


Fig. 177.—Sargent-type gas calorimeter. (American Meter Co.)

The gas is assumed to be saturated with water after passing through the water in the meter and pressure regulator. The observed volume is multiplied by a factor to reduce it to standard conditions. The magnitude of this correction factor may be obtained (to 0.01 %) from Table III in the Gas Calorimeter Tables. Or it may be calculated from the ideal gas laws:

$$\text{correction factor} = \frac{(P - E)(60 + 459.7)}{(t + 459.7)(30 - 0.5217)} \quad (2)$$

where  $P$  is the total gas pressure,  $E$  the vapor pressure of water at  $t^\circ\text{F}$ .

In a precise measurement of the heating value of a gas, the observed value must be corrected for humidity, heat loss, the effect of buoyancy of the air on the observed weight of water, and the difference between inlet-water temperature and room temperature. A discussion of these corrections and tables for evaluating some of them can be found in the Gas Calorimeter Tables. All tables in that publication have been computed for gas rates corresponding to 3000 B.t.u. per hour and 40 % of excess air. A well-fitted damper with two half-inch holes, when in the "closed" position will allow about 40 % of excess air to pass through the calorimeter when gas is burned at 3000 B.t.u. per hour.

Gas distributors are accustomed to base their rates on measurement of the heating value of the gas under the conditions in the meter. This gross heating value is given by

$$H = \frac{W(t_2 - t_1)}{V \left\{ \frac{17.64(h - a)}{460t_3} \right\}}$$

where  $H$  = B.t.u. per cubic foot of gas.

$W$  = weight of water in pounds.

$V$  = volume of gas (cu. ft.) as shown by meter.

$h$  = height of barometer in inches of mercury.

$t_1$  = temperature of inlet water,  $^\circ\text{F}$ .

$t_2$  = temperature of outlet water,  $^\circ\text{F}$ .

$t_3$  = temperature of gas at meter, °F.

$a$  = pressure of water vapor in inches of mercury at  $t_3$  °F.

### Procedure

With the gas valve at the burner closed, connect the gas supply through the meter and regulator. Notice whether the index of the meter moves. If it does, find the leak and remedy it. Start the flow of water through the calorimeter and then light the burner. Adjust the flow of water so the temperature change inside the calorimeter is about 15°F. Adjust the damper as mentioned above.

While waiting for the establishment of a steady thermal condition, prepare a data sheet<sup>2</sup> and record the preliminary observations: room temperature, barometric pressure, pressure and temperature of the gas in the meter, wet- and dry-bulb readings on the psychrometer, and temperature of the combustion products.

When all thermometers indicate nearly steady conditions, note simultaneously the meter reading and the inlet and outlet water temperatures. Immediately place beakers to receive the outlet water and condensate. Record thermometer readings every 30 seconds until about 2 liters of water have been collected. Then take a meter reading and remove the beakers. Determine  $M_w$  and  $M_s$  by weighing. Data are then available for calculating the heating value of the gas and for making the necessary corrections.

## EXPERIMENT 22

### Thermal Analysis

#### Object

Comparison and interpretation of cooling curves for a binary alloy and for the pure metals. Verification of the

<sup>2</sup> Pads of data sheets similar to the form recommended by the Bureau of Standards can be purchased from calorimeter supply companies.

essential features of the phase diagram for the Pb-Sn system. Thermal analysis of a Pb-Sn alloy of unknown composition. Practice in the use of a recording potentiometer.

### Apparatus

Electric furnace. Variable transformer. Gas furnace. Crucibles containing: lead; tin; Pb-Sn eutectic mixture, 62% Sn; alloy of 10% Sn; alloy of 20% Sn; and alloy of unknown composition. Labeled rack for crucibles. Thermocouples with pyrex protectors. Precision potentiometer.

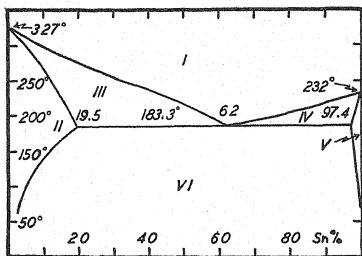


FIG. 178.—Pb-Sn equilibrium diagram. (J. Stockdale, *J. Inst. Metals*, 49, 267 (1932).)

Recording potentiometer. 2 batteries. Standard cell. 2 electric timers. Asbestos-lined iron pot. Crucible tongs. Ice-filled Dewar flask.

### Discussion

An equilibrium diagram of the Pb-Sn system is given in Fig. 178. From the cooling curves obtained in the laboratory it is desired to verify the following: (i) the melting point of Pb, (ii) the melting point of Sn, (iii) the composition of the eutectic mixture and the eutectic temperature, (iv) existence of a solid solution, region II of Fig. 178, (v) the limit of solubility of Sn in Pb.

Tin has three allotropic forms:  $\gamma$ , stable from 232 to 161°;  $\beta$ , stable from 161 to 18°; and  $\alpha$ , stable below 18°. The influence of these transformations does not appear to justify including additional horizontal lines indicating phase changes in the Pb-Sn diagram. Cooling curves of alloys containing 18 to 62% Sn may show an exothermic halt about 155°C. This was formerly included as a phase transformation. Now the change is attributed to supersaturation followed by sudden precipitation.

Temperatures at which changes of state occur are determined by any of the methods discussed in Chap. XI i.e., (i) ordinary cooling curve method, (ii) inverse-rate method, (iii) differential method, or (iv) derived differential method.

### Procedure

The recording potentiometer is used to obtain cooling curves for pure Sn and for pure Pb. Make the necessary external connections of battery and thermocouple to the potentiometer recorder. Standardize the potentiometer current and make any necessary internal adjustments only under supervision of the instructor. Heat one of the samples in the gas furnace. When molten, insert a thermocouple, protected by a pyrex tube. Turn off the gas and obtain a cooling curve, leaving the specimen in the furnace.

With the recording potentiometer in operation and requiring little attention, obtain cooling data for each of the remaining samples.

Finally, determine the composition of the unknown sample by comparing its phase change temperatures with the Pb-Sn phase diagram. To find on which side of the eutectic composition it lies, consult the instructor or make a rough determination of the density of the alloy.

1. On a Pb-Sn phase diagram, indicate (with colored lines) those features which you verified in the laboratory.

2. At the side of your Pb-Sn phase diagram, draw qualitative examples of cooling curves (temperature vs. time) that



would be obtained in cooling alloys of the following compositions: (a) 100% Pb, (b) 100% Sn, (c) 62% Sn and (d) 85% Sn.

3. A Pb-Sn alloy of 10% Sn is cooled from 350°C. to 0°C. Indicate all transitions that occur and the temperatures at which they occur.

4. For each of the areas that have been numbered (I-VI) in Fig. 178 state the number of phases present, the number of components, and identify the latter.

### EXPERIMENT 23

## Coefficient of Viscosity of a Gas

### Object

Determination of the viscosity of air at different temperatures by a constant volume method. Practice in the use of thermoregulators.

### Apparatus

Flask, capillary tube and mercury manometer, water bath, thermometer, heater, stirrer and thermoregulator. Cathetometer. Timer.

### Discussion

In the laminar (stream line) flow of a fluid the force  $F$  in the direction of flow acting on an area perpendicular to the direction is proportional to the area  $A$  and to the velocity gradient  $dv/dr$  across the stream:

$$F = \eta A \frac{dv}{dr} \quad (1)$$

is characteristic of the fluid and depends upon temperature. The coefficient of viscosity  $\eta$  is expressed in dyne sec. cm.<sup>-2</sup> or poises. Kinematic viscosity is the ratio of viscosity to density.

Poiseuille's formula for the flow of a liquid in a cylinder,

$$Q = \left( \frac{\pi R^4}{8L\eta} \right) (P_1 - P_2) \quad (2)$$

gives  $Q$ , the volume of fluid passing any cross section in unit time, in terms of the radius  $R$ , the length  $L$ , the difference between the pressures at the ends,  $P_1 - P_2$  and the coefficient of viscosity  $\eta$ . In the case of a gas the rate of flow past any section depends on the pressure there. Eq. 1 may, however, be applied to an element  $dx$  of the tube and then integrated. If this is done the relation<sup>1</sup> obtained is

$$\eta = \frac{(\pi R^4 / 8LV)Pt}{\log_e \left( \frac{p_2 + P}{p_1 + P} \frac{p_1 - P}{p_2 - P} \right)} \quad (3)$$

where  $V$  is the constant volume of gas at the entrance of the tube,  $p_1$  and  $p_2$  are the pressures at the entrance of the capillary at the beginning and end of  $t$  seconds of observation, respectively, and  $P$  is the atmospheric pressure.

The essential apparatus is sketched in Fig. 179.<sup>2</sup> An adjustable mercury column  $A$  is connected by flexible rubber tubing and a short section of glass tube with a ground glass joint to an inverted flask  $V$  of volume 300 ml. In an opening in the side of the glass tube is inserted one end of a capillary tube  $C$ . The other end of the capillary is fitted into a larger tube provided with a stopcock  $S$ . Air can be compressed in  $V$  by raising column  $A$ , and allowed to escape through the capillary for a time  $t$ . The volume of gas in the flask is kept constant by adjusting the column  $A$  to keep the mercury level at the fiducial mark  $F$ .

To permit measurement of the coefficient of gas viscosity at different temperatures, the flask and capillary tube are

<sup>1</sup> See, for example, B. L. Worsnop and H. T. Flint, *Advanced Practical Physics for Students*, New York: E. P. Dutton, 1923, pp. 174-7.

<sup>2</sup> R. L. Weber, *American Physics Teacher* 7, 163 (1939).

immersed in water contained in a copper-lined wood box. The temperature of the water bath is adjusted by a knife-

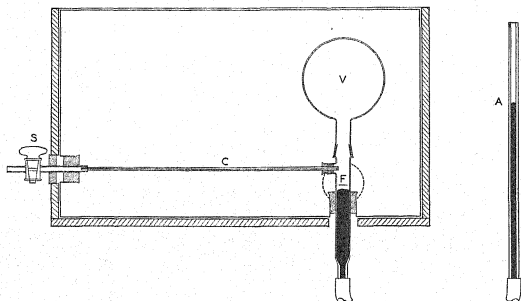


FIG. 179.—Diagram of viscosity apparatus.

type immersion heater, a bimetallic thermoregulator and a stirring motor (Fig. 180). Two glass windows cemented over circular openings in the sides of the tank permit observation

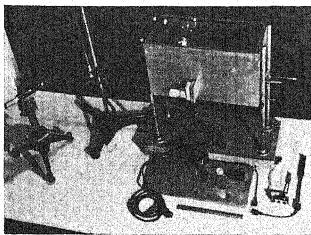


FIG. 180.—Details of constant temperature bath.

of the fiducial mark *F*, a small lamp being placed behind one window to provide illumination.

## Procedure

The capillary tubing should be tested for uniformity of bore by measuring the length of a short (1 cm.) thread of mercury at different positions in the tube. Its radius is then found indirectly by filling the tube with mercury and, from the weight and density of the mercury, calculating the volume of the capillary bore. The volume  $V$  of the flask is found by inverting it and filling it with distilled water to the reference mark  $F$ .

The following observations are needed: temperature of bath; cathetometer readings on mark  $F$ , on the mercury surface in the manometer at the beginning of a run, on that surface at the end of the run; time of flow; and barometric pressure. These data, together with the constant of the apparatus ( $\pi R^4/8LV$ ), are sufficient to determine the viscosity  $\eta$  from Eq. 3.

By using ice for the lowest temperature, measurements can be made over the temperature range from  $0^\circ\text{C}$ . to about  $60^\circ\text{C}$ . Values obtained for the coefficient of viscosity may be compared with Sutherland's formula<sup>3</sup> expressing its dependence on temperature,

$$\eta = \eta_0 \frac{T_0 + c}{T + c} \left( \frac{T}{T_0} \right)^{3/2} \quad (4)$$

where for air Sutherland's constant  $c = 120$  and  $\eta_{23} = 1822.6 \times 10^{-7}$ .

## EXPERIMENT 24

# The Curie Temperature of Nickel

## Object

A qualitative investigation of variation of ferromagnetic susceptibility with temperature. Determination of the Curie point for nickel of commercial purity.

<sup>3</sup> *International Critical Tables* (1929), vol. 5, p. 1.

### Apparatus

Nickel sample,  $N$  (Fig. 181). Furnace  $F$ . Thermocouple  $TC$ . Portable potentiometer  $P$ . Transformer  $T$ . Two variable transformers  $V$ . Copper-oxide rectifier  $CR$ . Ammeter  $A_1$ . Milliammeter  $A_2$ . Galvanometer  $G$ . Two 10,000-ohm dial decade resistance boxes  $R_1$  and  $R_2$ . Mercury thermometer. Timer.

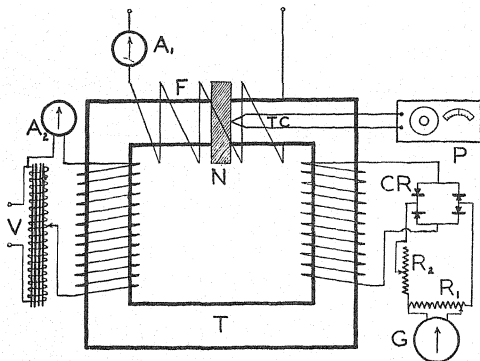


FIG. 181.—Curie point apparatus.

### Discussion

It is the purpose of this experiment to investigate the variation of ferromagnetic susceptibility with temperature. Without necessarily adopting a particular theory of the mechanism of ferromagnetism,<sup>1</sup> we may picture a magnetized ferromagnetic material as composed of magnetic "carriers" aligned as in Fig. 182*a*. If the sample is heated, we might expect the thermal motion imparted to the molecules would

<sup>1</sup> See, for example, C. E. Stoner, *Magnetism and Matter*, London: Methuen, 1934.

affect the molecular alignment, and with sufficient temperature rise would destroy their orderly state, resulting in the condition suggested by Fig. 182*b*. If there is a definite relationship between the energy of the magnetized state and the thermal energy necessary to remove the magnetism, this loss of magnetism should occur at a definite temperature for each material. P. Curie found (1895) that each ferromagnetic substance lost its ferromagnetism at a certain

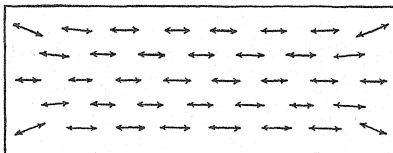


FIG. 182*a*.—Magnetic carriers aligned.

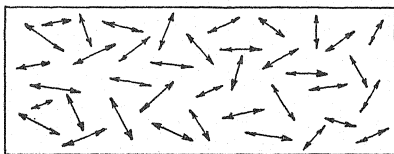


FIG. 182*b*.—Magnetic carriers in random orientation.

temperature, and that thereafter the small remaining susceptibility was inversely proportional to the temperature. That is, ferromagnetic materials become paramagnetic above the Curie temperature. Recent values for some Curie temperatures are: iron,  $770 \pm 5^\circ\text{C}.$ ; cobalt,  $1120 \pm 20^\circ\text{C}.$ ; nickel  $358 \pm 2^\circ\text{C}.$

### Procedure

If the sample of nickel is included as part of the magnetic circuit of a transformer, a simple method suggests itself for finding the Curie temperature of the nickel. As the nickel

is heated a constant alternating current is maintained in the transformer primary. Any change in the secondary current is then an indication of a change in the characteristics of the magnetic circuit. When the nickel loses its ferromagnetism there will be a marked decrease in the secondary current.

Connect the apparatus according to Fig. 181. The a.c. from the transformer secondary is changed to d.c. by a copper-

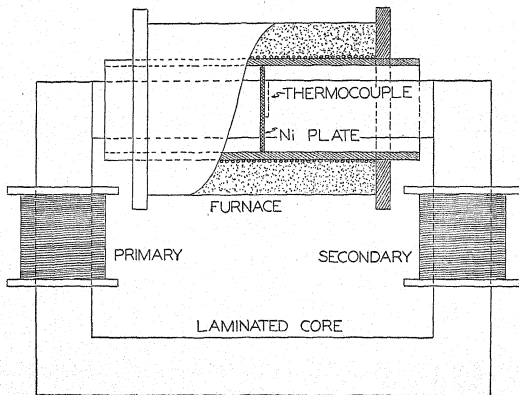


FIG. 183.—Curie point apparatus: details of furnace and transformer.

oxide rectifier  $CR$  and measured with a galvanometer  $G$ . The temperature of the nickel sample  $N$  is obtained with a calibrated thermocouple connected to a potentiometer  $P$ .

Connect the electric furnace through an ammeter and variable transformer to the a.c. line. Connect the primary of the transformer through a milliammeter and variable transformer to an a.c. source. When connections have been completed, set the galvanometer resistance  $R_2$  to 10,000 ohms, the turn on the primary current and adjust it to

0.5 amp. It is important that the current be kept constant throughout the experiment.

Check the zero reading of the galvanometer by setting the shunt resistance  $R_1$  to zero. Then by adjusting  $R_1$  bring the galvanometer to approximately half-scale reading. Turn on the furnace heating current. Notice and explain any immediate change in galvanometer reading.

Galvanometer readings will increase gradually as the furnace temperature rises to about 320–340°C., then decrease over the range 330–370°C., and finally begin to increase again for still higher temperatures. Potentiometer and galvanometer readings should be taken at intervals of about 25°C. up to 320°C. and then at 5°C. intervals. It will be well to turn off the furnace current momentarily while taking readings. (Why?)

After the furnace has reached a temperature of about 380°C. the heating current should be turned off and readings continued as the furnace cools. Plot a graph of galvanometer deflection vs. temperature for both increasing and decreasing temperatures. Indicate clearly the Curie point (or region) on each curve. Discuss any displacement of one curve with respect to the other.

On what basis would you explain the hysteresis or lag in the return of ferromagnetism to the nickel as the temperature decreases?

Changes in what other physical properties could be used to locate the Curie point of a metal?

A Jackson-Russell alloy of Fe-Ni-Cr-Si can be made with its Curie point at any temperature by varying its composition. Suggest how such an alloy could be used to protect generators from overheating, for automatic fire alarms, for air conditioning control and for controlling the temperature of a small laboratory furnace.







## Appendix

### Tables

1. Physical constants.
2. Temperature interconversion tables ( $^{\circ}\text{C} \leftrightarrow ^{\circ}\text{F}$ ).
3. The chemical elements.
4. Platinum to platinum + 10% rhodium thermocouple ( $^{\circ}\text{C}$ ).
5. Platinum to platinum + 10% rhodium thermocouple ( $^{\circ}\text{F}$ ).
6. Platinum to platinum + 13% rhodium thermocouple ( $^{\circ}\text{C}$ ).
7. Platinum to platinum + 13% rhodium thermocouple ( $^{\circ}\text{F}$ ).
8. Chromel-Alumel thermocouple ( $^{\circ}\text{C}$ ).
9. Chromel-Alumel thermocouple ( $^{\circ}\text{F}$ ).
10. Copper-constantan thermocouple ( $^{\circ}\text{C}$ ).
11. Copper-constantan thermocouple ( $^{\circ}\text{F}$ ).
12. Iron-constantan thermocouple ( $^{\circ}\text{C}$ ).
13. Iron-constantan thermocouple ( $^{\circ}\text{F}$ ).
14. Thermal e.m.f. of important thermocouple materials relative to platinum.
15. Thermal e.m.f. of some alloys relative to platinum.
16. Electrical resistivity as a function of temperature.
17. Spectral emissivity of materials, surface unoxidized.
18. Spectral emissivity of oxides.
19. Total emissivity of metals, surface unoxidized.
20. Total emissivity of miscellaneous materials.
21. True temperatures corresponding to various emissivities and various brightness temperatures.
22. Properties of tungsten.
23. Relative humidity from wet- and dry-bulb thermometer readings.
24. Pressure of saturated water vapor.

TABLE I\*

PHYSICAL CONSTANTS<sup>1</sup>

Wien-Planck constants	$c_1 = (3.732 \pm 0.006) \times 10^{-5} \text{ erg cm.}^2 \text{ sec.}^{-1}$ $c_2 = 1.436 \pm 0.001 \text{ cm. deg.}$ $\lambda_m T = (2892 \pm 2) \times 10^{-4} \text{ cm. deg.}$ $\nu_m T = (5890 \pm 4) \times 10^7 \text{ deg.}^{-1} \text{ sec.}^{-1}$
Stefan-Boltzmann constant	$\sigma = (5.70 \pm 0.2) \times 10^{-5} \text{ erg sec.}^{-1} \text{ cm.}^{-2} \text{ deg.}^{-4}$
Velocity of light	$c = (2.9978 \pm 0.0002) \times 10^{10} \text{ cm. sec.}^{-1}$
Faraday constant	$F = (2.8926 \pm 0.0003) \times 10^{-14} \text{ (esu) mole}^{-1}$
Ice point	$T_0 = 273.165 \pm 0.015^\circ \text{K.}^2$
Gas constant	$R = (8.3142 \pm 0.0010) \times 10^7 \text{ erg deg.}^{-1} \text{ mole}^{-1}$ $R = 1.98714 \pm 0.00019 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
Boltzmann constant	$k = (1.380 \pm 0.002) \times 10^{-16} \text{ erg deg.}^{-1}$
Electronic charge	$e = (4.800 \pm 0.004) \times 10^{-10} \text{ (esu)}$
Specific electronic charge	$e/m = (5.273 \pm 0.002) \times 10^{17} \text{ (esu) g}^{-1}$
Planck's constant	$h = (6.61 \pm 0.01) \times 10^{-27} \text{ erg sec.}$ $h/e = (1.377 \pm 0.001) \times 10^{-17} \text{ erg sec. (esu)}^{-1}$
Least mechanical equivalent of light	$M = (151 \pm 1) \times 10^{-5} \text{ watt ("new" lumen)}^{-1}$
Conversion factors	1 Int. ohm = 1.00048 Abs. ohm 1 Int. volt = 1.00034 Abs. volt 1 Int. ampere = 0.99986 Abs. ampere 1 calorie = 4.1833 Int. joule 1 calorie = 4.1841 Abs. joule
Avogadro's number	$N = 6.0244 \times 10^{23}$
Loschmidt's number	$N = 2.6878 \times 10^{19}$

\* Unless otherwise credited, these tables are taken by permission from *Temperature—Its Measurement and Control in Science and Industry*. New York: Reinhold, 1941.

<sup>1</sup> H. T. Wensel, *J. Research Nat. Bur. Standards*, **22**, 373 (1939).

F. D. Rossini, " . . . Constants being used by . . . the National Bureau of Standards, as of January 1, 1939."

<sup>2</sup> J. A. Beattie in "Temperature—Its Measurement and Control . . ." p. 87; see also *Nature*, **145**, 597 (1940).

TABLE II  
TEMPERATURE INTERCONVERSION TABLES ( $^{\circ}\text{C} \longleftrightarrow ^{\circ}\text{F}$ .) AND MELTING  
POINTS OF THE CHEMICAL ELEMENTS<sup>1</sup>  
Conversion table: degrees centigrade to degrees Fahrenheit

$^{\circ}\text{C}.$	0	10	20	30	40	50	60	70	80	90		
	F	F	F	F	F	F	F	F	F	F		
-200	-328	-346	-364	-382	-400	-418	-436	-454	-472	-490		
-100	-148	-166	-184	-202	-220	-238	-256	-274	-292	-310		
-0	+32	+14	-4	-22	-40	-58	-76	-94	-112	-130		
0	32	50	68	86	104	122	140	158	176	194	$^{\circ}\text{C}.$	$^{\circ}\text{F}.$
100	212	230	248	266	284	302	320	338	356	374	1	1.8
200	392	410	428	446	464	482	500	518	536	554	2	3.6
300	572	590	608	626	644	662	680	698	716	734	3	5.4
400	752	770	788	806	824	842	860	878	896	914	4	7.2
500	932	950	968	986	1004	1022	1040	1058	1076	1094	5	9.0
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274	6	10.8
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454	7	12.6
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634	8	14.4
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814	9	16.2
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994		
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174	10	18.0
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354		
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534		
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714		
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894		
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074	$^{\circ}\text{F}.$	$^{\circ}\text{C}.$
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254	1	0.56
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434	2	1.11
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614	3	1.67
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794	4	2.22
2100	3812	3830	3848	3866	3884	3902	3920	3938	3956	3974	5	2.78
2200	3992	4010	4028	4046	4064	4082	4100	4118	4136	4154	6	3.33
2300	4172	4190	4208	4226	4244	4262	4280	4298	4316	4334	7	3.80
2400	4352	4370	4388	4406	4424	4442	4460	4478	4496	4514	8	4.44
2500	4532	4550	4568	4586	4604	4622	4640	4658	4676	4694	9	5.00
2600	4712	4730	4748	4766	4784	4802	4820	4838	4856	4874		
2700	4892	4910	4928	4946	4964	4982	5000	5018	5036	5054	10	5.56
2800	5072	5090	5108	5126	5144	5162	5180	5198	5216	5234	11	6.11
2900	5252	5270	5288	5306	5324	5342	5360	5378	5396	5414	12	6.07
3000	5432	5450	5468	5486	5504	5522	5540	5558	5576	5594	13	7.22
3100	5612	5630	5648	5666	5684	5702	5720	5738	5756	5774	14	7.78
3200	5792	5810	5828	5846	5864	5882	5900	5918	5936	5954	15	8.33
3300	5972	5990	6008	6026	6044	6062	6080	6098	6116	6134	16	8.89
3400	6152	6170	6188	6206	6224	6242	6260	6278	6296	6314	17	9.44
3500	6332	6350	6368	6386	6404	6422	6440	6458	6476	6494		
3600	6512	6530	6548	6566	6584	6602	6620	6638	6656	6674	18	100.00
3700	6692	6710	6728	6746	6764	6782	6800	6818	6836	6854		
3800	6872	6890	6908	6926	6944	6962	6980	6998	7016	7034		
3900	7052	7070	7088	7106	7124	7142	7160	7178	7196	7214		
$^{\circ}\text{C}.$	0	10	20	30	40	50	60	70	80	90		

Examples:  $1347^{\circ}\text{C} = 2444^{\circ}\text{F} + 12.6^{\circ}\text{F} = 2456.6^{\circ}\text{F}$ .  $3367^{\circ}\text{F} = 1850^{\circ}\text{C} + 2.78^{\circ}\text{C} = 1852.78^{\circ}\text{C}$ .

<sup>1</sup> Nat. Bur. Standards misc. pub. M126 (1937).

TABLE II.—(Continued)

Conversion table: degrees Fahrenheit to degrees centigrade  
(Single boldface figures indicate recurring decimals)

°F.	0	10	20	30	40	50	60	70	80	90	
	C	C	C	C	C	C	C	C	C	C	
-400	-240.0	-245.5	-251.1	-256.6	-262.2	-267.7	-273.2	-278.7	-284.2	-289.7	
-300	-184.4	-190.0	-195.5	-201.1	-206.6	-212.2	-217.7	-223.2	-228.7	-234.2	
-200	-128.8	-134.4	-140.0	-145.5	-151.1	-156.6	-162.2	-167.7	-173.2	-178.7	
-100	-73.3	-78.8	-84.4	-90.0	-95.5	-101.1	-106.6	-112.2	-117.7	-123.2	
-0	-17.7	-23.3	-28.8	-34.4	-40.0	-45.5	-51.1	-56.6	-62.2	-67.7	
0	-17.7	-12.2	-6.6	-1.1	+4.4	+10.0	+15.5	+21.1	+26.6	+32.2	
100	37.7	43.3	48.8	54.4	60.0	65.5	71.1	76.6	82.2	87.7	
200	93.3	98.8	104.4	110.0	115.5	121.1	126.6	132.2	137.7	143.3	
300	148.8	154.4	160.0	165.5	171.1	176.6	182.2	187.7	193.2	198.7	
400	204.4	210.0	215.5	221.1	226.6	232.2	237.7	243.2	248.7	254.2	
500	260.0	265.5	271.1	276.6	282.2	287.7	293.2	298.7	304.2	310.0	
600	315.5	321.1	326.6	332.2	337.7	343.2	348.7	354.2	360.0	365.5	
700	371.1	376.6	382.2	387.7	393.2	398.7	404.2	410.0	415.5	421.1	
800	426.6	432.2	437.7	443.2	448.7	454.2	460.0	465.5	471.1	476.6	
900	482.2	487.7	493.2	498.7	504.2	510.0	515.5	521.1	526.6	532.2	
1000	537.7	543.2	548.7	554.2	560.0	565.5	571.1	576.6	582.2	587.7	°F. °C.
1100	593.2	598.7	604.2	610.0	615.5	621.1	626.6	632.2	637.7	643.2	1 0.5
1200	648.7	654.2	660.0	665.5	671.1	676.6	682.2	687.7	693.2	698.7	2 1.1
1300	704.2	710.0	715.5	721.1	726.6	732.2	737.7	743.2	748.7	754.2	3 1.6
1400	760.0	765.5	771.1	776.6	782.2	787.7	793.2	798.7	804.2	810.0	
1500	815.5	821.1	826.6	832.2	837.7	843.2	848.7	854.2	860.0	865.5	
1600	871.1	876.6	882.2	887.7	893.2	898.7	904.2	910.0	915.5	921.1	4 2.2
1700	926.6	932.2	937.7	943.2	948.7	954.2	960.0	965.5	971.1	976.6	5 2.7
1800	982.2	987.7	993.2	998.7	1004.2	1010.0	1015.5	1021.1	1026.6	1032.2	6 3.3
1900	1037.7	1043.2	1048.7	1054.2	1060.0	1065.5	1071.1	1076.6	1082.2	1087.7	7 3.8
2000	1093.2	1098.7	1104.2	1110.0	1115.5	1121.1	1126.6	1132.2	1137.7	1143.2	8 4.4
2100	1148.7	1154.2	1160.0	1165.5	1171.1	1176.6	1182.2	1187.7	1193.2	1198.7	9 5.0
2200	1204.2	1210.0	1215.5	1221.1	1226.6	1232.2	1237.7	1243.2	1248.7	1254.2	
2300	1260.0	1265.5	1271.1	1276.6	1282.2	1287.7	1293.2	1298.7	1304.2	1310.0	
2400	1315.5	1321.1	1326.6	1332.2	1337.7	1343.2	1348.7	1354.2	1360.0	1365.5	
2500	1371.1	1376.6	1382.2	1387.7	1393.2	1398.7	1404.2	1410.0	1415.5	1421.1	
2600	1426.6	1432.2	1437.7	1443.2	1448.7	1454.2	1460.0	1465.5	1471.1	1476.6	
2700	1482.2	1487.7	1493.2	1498.7	1504.2	1510.0	1515.5	1521.1	1526.6	1532.2	
2800	1537.7	1543.2	1548.7	1554.2	1560.0	1565.5	1571.1	1576.6	1582.2	1587.7	
2900	1593.2	1598.7	1604.2	1610.0	1615.5	1621.1	1626.6	1632.2	1637.7	1643.2	
3000	1648.7	1654.2	1660.0	1665.5	1671.1	1676.6	1682.2	1687.7	1693.2	1698.7	
3100	1704.2	1710.0	1715.5	1721.1	1726.6	1732.2	1737.7	1743.2	1748.7	1754.2	
3200	1760.0	1765.5	1771.1	1776.6	1782.2	1787.7	1793.2	1798.7	1804.2	1810.0	
3300	1815.5	1821.1	1826.6	1832.2	1837.7	1843.2	1848.7	1854.2	1860.0	1865.5	
3400	1871.1	1876.6	1882.2	1887.7	1893.2	1898.7	1904.2	1910.0	1915.5	1921.1	
3500	1926.6	1932.2	1937.7	1943.2	1948.7	1954.2	1960.0	1965.5	1971.1	1976.6	
3600	1982.2	1987.7	1993.2	1998.7	2004.2	2010.0	2015.5	2021.1	2026.6	2032.2	
°F.	0	10	20	30	40	50	60	70	80	90	

Examples:  $-246.0^{\circ}\text{F.} = -151.1^{\circ}\text{C.} - 3.33^{\circ}\text{C.} = -154.44^{\circ}\text{C.}$

$3762^{\circ}\text{F.} = 2071.1^{\circ}\text{C.} + 1.1^{\circ}\text{C.} = 2072.2^{\circ}\text{C.}$

$2423.5^{\circ}\text{F.} = 1326.66^{\circ}\text{C.} + 1.66^{\circ}\text{C.} + 0.27^{\circ}\text{C.} = 1328.61^{\circ}\text{C.}$

TABLE II.—(Continued)  
°F. to °C.

°F.	0	10	20	30	40	50	60	70	80	90	
	C	C	C	C	C	C	C	C	C	C	
3700	2037.7	2043.3	2048.8	2054.4	2060.0	2065.5	2071.1	2076.6	2082.2	2087.7	
3800	2093.3	2098.8	2104.4	2110.0	2115.5	2121.1	2126.6	2132.2	2137.7	2143.3	
3900	2148.8	2154.4	2160.0	2165.5	2171.1	2176.6	2182.2	2187.7	2193.3	2198.8	
4000	2204.4	2210.0	2215.5	2221.1	2226.6	2232.2	2237.7	2243.3	2248.8	2254.4	
4100	2260.0	2265.5	2271.1	2276.6	2282.2	2287.7	2293.3	2298.8	2304.4	2310.0	
4200	2315.5	2321.1	2326.6	2332.2	2337.7	2343.3	2348.8	2354.4	2360.0	2365.5	
4300	2371.1	2376.6	2382.2	2387.7	2393.3	2398.8	2404.4	2410.0	2415.5	2421.1	
4400	2426.6	2432.2	2437.7	2443.3	2448.8	2454.4	2460.0	2465.5	2471.1	2476.6	
4500	2482.2	2487.7	2493.3	2498.8	2504.4	2510.0	2515.5	2521.1	2526.6	2532.2	
4600	2537.7	2543.3	2548.8	2554.4	2560.0	2565.5	2571.1	2576.6	2582.2	2587.7	
4700	2593.3	2598.8	2604.4	2610.0	2615.5	2621.1	2626.6	2632.2	2637.7	2643.3	
4800	2648.8	2654.4	2660.0	2665.5	2671.1	2676.6	2682.2	2687.7	2693.3	2698.8	
4900	2704.4	2710.0	2715.5	2721.1	2726.6	2732.2	2737.7	2743.3	2748.8	2754.4	
5000	2760.0	2765.5	2771.1	2776.6	2782.2	2787.7	2793.3	2798.8	2804.4	2810.0	°F. °C.
5100	2815.5	2821.1	2826.6	2832.2	2837.7	2843.3	2848.8	2854.4	2860.0	2865.5	1 0.5
5200	2871.1	2876.6	2882.2	2887.7	2893.3	2898.8	2904.4	2910.0	2915.5	2921.1	2 1.1
5300	2926.6	2932.2	2937.7	2943.3	2948.8	2954.4	2960.0	2965.5	2971.1	2976.6	3 1.6
5400	2982.2	2987.7	2993.3	2998.8	3004.4	3010.0	3015.5	3021.1	3026.6	3032.2	4 2.2
5500	3037.7	3043.3	3048.8	3054.4	3060.0	3065.5	3071.1	3076.6	3082.2	3087.7	5 2.7
5600	3093.3	3098.8	3104.4	3110.0	3115.5	3121.1	3126.6	3132.2	3137.7	3143.3	6 3.3
5700	3148.8	3154.4	3160.0	3165.5	3171.1	3176.6	3182.2	3187.7	3193.3	3198.8	7 3.8
5800	3204.4	3210.0	3215.5	3221.1	3226.6	3232.2	3237.7	3243.3	3248.8	3254.4	8 4.4
5900	3260.0	3265.5	3271.1	3276.6	3282.2	3287.7	3293.3	3298.8	3304.4	3310.0	9 5.0
6000	3315.5	3321.1	3326.6	3332.2	3337.7	3343.3	3348.8	3354.4	3360.0	3365.5	
6100	3371.1	3376.6	3382.2	3387.7	3393.3	3398.8	3404.4	3410.0	3415.5	3421.1	
6200	3426.6	3432.2	3437.7	3443.3	3448.8	3454.4	3460.0	3465.5	3471.1	3476.6	
6300	3482.2	3487.7	3493.3	3498.8	3504.4	3510.0	3515.5	3521.1	3526.6	3532.2	
6400	3537.7	3543.3	3548.8	3554.4	3560.0	3565.5	3571.1	3576.6	3582.2	3587.7	
6500	3593.3	3598.8	3604.4	3610.0	3615.5	3621.1	3626.6	3632.2	3637.7	3643.3	
6600	3648.8	3654.4	3660.0	3665.5	3671.1	3676.6	3682.2	3687.7	3693.3	3698.8	
6700	3704.4	3710.0	3715.5	3721.1	3726.6	3732.2	3737.7	3743.3	3748.8	3754.4	
6800	3760.0	3765.5	3771.1	3776.6	3782.2	3787.7	3793.3	3798.8	3804.4	3810.0	
6900	3815.5	3821.1	3826.6	3832.2	3837.7	3843.3	3848.8	3854.4	3860.0	3865.5	
7000	3871.1	3876.6	3882.2	3887.7	3893.3	3898.8	3904.4	3910.0	3915.5	3921.1	
7100	3926.6	3932.2	3937.7	3943.3	3948.8	3954.4	3960.0	3965.5	3971.1	3976.6	
7200	3982.2	3987.7	3993.3	3998.8	4004.4	4010.0	4015.5	4021.1	4026.6	4032.2	
7300	4037.7	4043.3	4048.8	4054.4	4060.0	4065.5	4071.1	4076.6	4082.2	4087.7	
7400	4093.3	4098.8	4104.4	4110.0	4115.5	4121.1	4126.6	4132.2	4137.7	4143.3	
7500	4148.8	4154.4	4160.0	4165.5	4171.1	4176.6	4182.2	4187.7	4193.3	4198.8	
7600	4204.4	4210.0	4215.5	4221.1	4226.6	4232.2	4237.7	4243.3	4248.8	4254.4	
7700	4260.0	4265.5	4271.1	4276.6	4282.2	4287.7	4293.3	4298.8	4304.4	4310.0	
7800	4315.5	4321.1	4326.6	4332.2	4337.7	4343.3	4348.8	4354.4	4360.0	4365.5	
7900	4371.1	4376.6	4382.2	4387.7	4393.3	4398.8	4404.4	4410.0	4415.5	4421.1	
°F.	0	10	20	30	40	50	60	70	80	90	

TABLE III

THE CHEMICAL ELEMENTS: THEIR ATOMIC NUMBERS, SYMBOLS, AND WEIGHTS, AND THEIR MELTING POINTS ON THE INTERNATIONAL TEMPERATURE SCALE<sup>1</sup>

[For International Temperature Scale see *Bur. Standards J. Research* 1, 635 (1928) RP22]

Temperatures below  $-190^{\circ}\text{C.}$  are on the Centigrade Thermodynamic Scale.

The atomic weights given constitute the complete list of the International Weights of 1936, as approved and reported by the Committee on Atomic Weights of the International Union of Chemistry. There is reason to believe that the following (unofficial) values may prove more nearly correct: Aluminum, 26.974; carbon, 12.009; gallium, 69.74.

Atomic number	Atomic symbol	Name of element	Melting point, $^{\circ}\text{C.}$	Atomic weight
89	Ac	Actinium.....	"1600	
13	Al	Aluminum.....	660.0 $\pm$ 0.1	26.97
51	Sb	Antimony.....	630.5 $\pm$ 0.1	121.76
18	A	Argon.....	-189.3 $\pm$ 0.5	39.944
33	As	Arsenic.....	"814	74.91
56	Ba	Barium.....	704 $\pm$ 20	137.36
4	Be	Beryllium.....	1280 $\pm$ 40	9.02
83	Bi	Bismuth.....	271.3 $\pm$ 0.1	209.00
5	B	Boron.....	2300 $\pm$ 300	10.82
35	Br	Bromine.....	-7.2 $\pm$ 0.2	79.916
48	Cd	Cadmium.....	320.0 $\pm$ 0.1	112.41
20	Ca	Calcium.....	850 $\pm$ 20	40.08
6	C	Carbon.....	3700 $\pm$ 100	12.00
58	Ce	Cerium.....	600 $\pm$ 50	140.13
55	Cs	Cesium.....	28 $\pm$ 2	132.91
17	Cl	Chlorine.....	-101 $\pm$ 2	35.457
24	Cr	Chromium.....	1800 $\pm$ 50	52.01
27	Co	Cobalt.....	1490 $\pm$ 20	58.94
41	Cb	Columbium.....	2000 $\pm$ 50	92.91
29	Cu	Copper.....	1083.0 $\pm$ 0.1	63.57
66	Dy	Dysprosium.....		162.46
68	Er	Erbium.....		167.64
63	Eu	Europium.....		152.0
9	F	Fluorine.....	-223 $\pm$ 10	19.00
64	Gd	Gadolinium.....		157.3
31	Ga	Gallium.....	29.78 $\pm$ 0.02	69.72
32	Ge	Germanium.....	958 $\pm$ 10	72.60
79	Au	Gold.....	1063.0 $\pm$ 0.0	197.2
72	Hf	Hafnium.....	"1700	178.6
2	He	Helium.....	-271.4 $\pm$ 0.2	4.002
67	Ho	Holmium.....		165.5
1	H	Hydrogen.....	-259.2 $\pm$ 0.1	1.0078
		H <sub>2</sub> (normal).....	-259.2 $\pm$ 0.1	
		HD.....	-256.5 $\pm$ 0.2	
		D <sub>2</sub> (normal).....	-254.5 $\pm$ 0.2	
61	Il	Illinium.....		
49	In	Indium.....	156.4 $\pm$ 0.1	114.76
53	I	Iodine.....	114 $\pm$ 1	126.92
77	Ir	Iridium.....	2454 $\pm$ 3	193.1
26	Fe	Iron.....	1535 $\pm$ 3	55.84
36	Kr	Krypton.....	-157 $\pm$ 0.5	83.7

TABLE III.—(Continued)

Atomic number	Atomic symbol	Name of element	Melting point, °C.	Atomic weight
57	La	Lanthanum.....	826 ± 5	138.92
82	Pb	Lead.....	327.4 ± 0.1	207.22
3	Li	Lithium.....	186 ± 5	6.940
71	Lu	Lutetium.....		175.0
12	Mg	Magnesium.....	650 ± 2	24.32
25	Mn	Manganese.....	1260 ± 20	54.93
43	Ma	Masturium.....	<sup>a</sup> 2700	
80	Hg	Mercury.....	-38.87 ± 0.02	200.61
42	Mo	Molybdenum.....	2025 ± 50	96.0
60	Nd	Neodymium.....	840 ± 40	144.27
10	Ne	Neon.....	-248.6 ± 0.3	20.183
28	Ni	Nickel.....	1455 ± 1	58.69
7	N	Nitrogen.....	-210.0 ± 0.3	14.008
76	Os	Osmium.....	2700 ± 200	191.5
8	O	Oxygen.....	-218.8 ± 0.3	16.0000
46	Pd	Palladium.....	1554 ± 1	106.7
15	P	Phosphorus, Y.....	44.1 ± 0.1	31.02
		Phosphorus, R.....	<sup>a</sup> 590	
78	Pt	Platinum.....	1773.5 ± 1	195.23
84	Po	Polonium.....	<sup>a</sup> 900	
19	K	Potassium.....	63 ± 1	39.096
59	Pr	Praseodymium.....	940 ± 50	140.92
91	Pa	Protactinium.....	<sup>a</sup> 3000	231
88	Ra	Radium.....	700	226.05
86	Rn	Radon.....	-71	222
75	Re	Rhenium.....	<sup>a</sup> 3000	186.31
45	Rh	Rhodium.....	1966 ± 3	102.91
37	Rb	Rubidium.....	39 ± 1	85.44
44	Ru	Ruthenium.....	2500 ± 100	101.7
62	Sm	Samarium.....	> 1300	150.43
21	Sc	Scandium.....	1200	45.10
34	Se	Selenium.....	220 ± 5	78.96
14	Si	Silicon.....	1430 ± 20	28.06
47	Ag	Silver.....	960.5 ± 0.0	107.880
11	Na	Sodium.....	97.7 ± 0.2	22.997
38	Sr	Strontium.....	770 ± 10	87.63
16	S	Sulfur:		32.06
		Monoclinic.....	119.2 ± 0.2	
		Rhombic.....	112.8 ± 0.2	
73	Ta	Tantalum.....	3000 ± 100	180.88
52	Te	Tellurium.....	450 ± 10	127.61
65	Tb	Terbium.....	327 ± 5	159.2
81	Tl	Thallium.....	300 ± 3	204.39
90	Th	Thorium.....	1800 ± 150	232.12
69	Tm	Thulium.....		169.4
50	Sn	Tin.....	231.9 ± 0.1	118.70
22	Ti	Titanium.....	1820 ± 100	47.90
74	W	Tungsten.....	3410 ± 20	184.0
92	U	Uranium.....	<sup>a</sup> 3600	238.14
23	V	Vanadium.....	1735 ± 50	50.95
54	Xe	Xenon.....	-112 ± 1	131.3
70	Yb	Ytterbium.....		173.04
39	Y	Yttrium.....	1490 ± 200	88.92
30	Zn	Zinc.....	419.5 ± 0.1	65.38
40	Zr	Zirconium.....	1750 ± 700	91.22
85	.....	Element 85.....	<sup>a</sup> 250	
87	.....	Element 87.....	<sup>a</sup> 23	

<sup>a</sup> Computed. <sup>b</sup> At 86 atmospheres. <sup>c</sup> At 30 atmospheres. <sup>d</sup> At 43 atmospheres.<sup>1</sup> Nat. Bur. Standards misc. pub. M126 (1937).



TABLE IV  
PLAT. VS. PLAT. + 10% RHODIUM THERMOCOUPLE<sup>1</sup>  
Degrees Centigrade, Reference Junction 0°C.

Deg. C.	0°	100°	200°	300°	400°	500°	600°	700°	800°
0°	0	.043	1.436	2.316	3.251	4.219	5.222	6.260	7.330
2°	.011	.668	1.453	2.334	3.270	4.239	5.243	6.281	7.352
4°	.023	.672	1.470	2.352	3.289	4.258	5.263	6.302	7.374
6°	.034	.687	1.487	2.370	3.308	4.278	5.284	6.323	7.396
8°	.046	.702	1.504	2.388	3.327	4.298	5.304	6.344	7.417
10°	.057	.717	1.521	2.406	3.346	4.318	5.325	6.365	7.439
12°	.068	.732	1.538	2.425	3.365	4.337	5.345	6.387	7.461
14°	.080	.747	1.555	2.443	3.384	4.357	5.366	6.408	7.483
16°	.091	.762	1.572	2.462	3.403	4.377	5.386	6.429	7.505
18°	.103	.777	1.589	2.480	3.422	4.397	5.407	6.450	7.527
20°	.114	.792	1.606	2.498	3.441	4.417	5.427	6.471	7.548
22°	.126	.807	1.623	2.517	3.461	4.436	5.448	6.493	7.570
24°	.138	.822	1.641	2.536	3.480	4.456	5.469	6.514	7.592
26°	.150	.838	1.658	2.554	3.499	4.476	5.489	6.535	7.614
28°	.162	.853	1.675	2.573	3.519	4.496	5.510	6.556	7.636
30°	.174	.869	1.692	2.591	3.538	4.516	5.530	6.578	7.658
32°	.186	.884	1.710	2.610	3.557	4.536	5.551	6.599	7.680
34°	.198	.899	1.727	2.628	3.577	4.556	5.571	6.620	7.702
36°	.211	.915	1.744	2.647	3.596	4.576	5.592	6.642	7.724
38°	.223	.931	1.762	2.665	3.615	4.596	5.613	6.663	7.746
40°	.235	.946	1.779	2.684	3.634	4.616	5.633	6.684	7.768
42°	.248	.962	1.797	2.703	3.653	4.636	5.654	6.706	7.790
44°	.260	.977	1.814	2.721	3.673	4.656	5.675	6.727	7.812
46°	.273	.993	1.832	2.740	3.692	4.676	5.696	6.748	7.834
48°	.286	1.009	1.850	2.759	3.711	4.696	5.717	6.769	7.856
50°	.299	1.025	1.867	2.778	3.731	4.716	5.737	6.790	7.878
52°	.312	1.041	1.885	2.796	3.750	4.736	5.758	6.812	7.900
54°	.325	1.057	1.902	2.815	3.770	4.756	5.779	6.834	7.922
56°	.338	1.073	1.920	2.834	3.789	4.776	5.800	6.855	7.944
58°	.351	1.089	1.938	2.852	3.808	4.796	5.821	6.877	7.966
60°	.365	1.105	1.956	2.871	3.828	4.817	5.841	6.898	7.989
62°	.378	1.121	1.973	2.890	3.847	4.837	5.862	6.920	8.011
64°	.391	1.137	1.991	2.909	3.867	4.857	5.883	6.941	8.033
66°	.405	1.154	2.009	2.928	3.886	4.877	5.904	6.963	8.055
68°	.418	1.170	2.027	2.947	3.906	4.897	5.925	6.984	8.077
70°	.432	1.186	2.045	2.965	3.925	4.918	5.945	7.005	8.100
72°	.445	1.203	2.063	2.984	3.945	4.938	5.966	7.027	8.122
74°	.459	1.219	2.081	3.003	3.964	4.958	5.987	7.049	8.144
76°	.473	1.236	2.099	3.022	3.984	4.978	6.008	7.070	8.166
78°	.487	1.252	2.117	3.041	4.003	4.998	6.029	7.092	8.188
80°	.500	1.269	2.134	3.060	4.023	5.019	6.050	7.113	8.211
82°	.514	1.285	2.152	3.079	4.042	5.039	6.071	7.135	8.233
84°	.528	1.302	2.170	3.098	4.062	5.059	6.092	7.157	8.255
86°	.542	1.318	2.189	3.117	4.081	5.080	6.113	7.179	8.277
88°	.557	1.335	2.207	3.136	4.101	5.100	6.134	7.200	8.300
90°	.571	1.352	2.225	3.155	4.121	5.120	6.155	7.222	8.322
92°	.585	1.368	2.243	3.174	4.140	5.141	6.176	7.244	8.344
94°	.600	1.385	2.261	3.193	4.160	5.161	6.197	7.265	8.367
96°	.614	1.402	2.279	3.212	4.180	5.182	6.218	7.287	8.389
98°	.629	1.419	2.297	3.232	4.200	5.202	6.239	7.309	8.411
100°	.643	1.436	2.316	3.251	4.219	5.222	6.260	7.330	8.434
M.V. per °C.	.00643	.00793	.00880	.00935	.00968	.0100	.0104	.0107	.0110

<sup>1</sup> Leeds & Northrup Std. 21031.See also W. F. Roeser and H. T. Wensel, *Bur. Standards J. Research*, 10, 275 (1933).

TABLE IV.—(Continued)

Deg. C.	900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°	1700°
	Millivolts								
0°	8.434	9.569	10.736	11.924	13.120	14.312	15.498	16.674	17.841
2°	8.456	9.592	10.759	11.948	13.144	14.336	15.521	16.698	17.864
4°	8.479	9.615	10.783	11.972	13.168	14.360	15.545	16.721	17.887
6°	8.501	9.638	10.807	11.995	13.192	14.383	15.569	16.744	17.910
8°	8.523	9.661	10.830	12.019	13.216	14.407	15.592	16.768	17.934
10°	8.546	9.685	10.854	12.043	13.239	14.431	15.615	16.792	17.957
12°	8.568	9.708	10.878	12.067	13.263	14.455	15.639	16.815	17.980
14°	8.591	9.731	10.901	12.091	13.287	14.479	15.663	16.838	18.004
16°	8.613	9.754	10.925	12.115	13.311	14.502	15.687	16.861	18.027
18°	8.636	9.777	10.949	12.139	13.335	14.526	15.710	16.885	18.050
20°	8.658	9.800	10.973	12.163	13.358	14.550	15.733	16.908	18.073
22°	8.681	9.823	10.996	12.187	13.382	14.574	15.757	16.932	—
24°	8.703	9.846	11.020	12.211	13.406	14.597	15.781	16.955	—
26°	8.726	9.869	11.044	12.235	13.430	14.621	15.805	16.978	—
28°	8.748	9.893	11.067	12.259	13.454	14.645	15.828	17.002	—
30°	8.771	9.916	11.091	12.283	13.478	14.668	15.852	17.026	—
32°	8.794	9.939	11.115	12.307	13.502	14.692	15.875	17.049	—
34°	8.816	9.962	11.139	12.330	13.526	14.716	15.899	17.072	—
36°	8.839	9.985	11.162	12.354	13.550	14.740	15.923	17.095	—
38°	8.861	10.009	11.186	12.378	13.574	14.764	15.946	17.119	—
40°	8.884	10.033	11.209	12.402	13.598	14.787	15.969	17.142	—
42°	8.907	10.056	11.233	12.426	13.621	14.811	15.993	17.165	—
44°	8.929	10.079	11.257	12.450	13.645	14.835	16.017	17.189	—
46°	8.952	10.102	11.281	12.474	13.669	14.859	16.040	17.212	—
48°	8.975	10.125	11.305	12.498	13.693	14.882	16.064	17.235	—
50°	8.998	10.149	11.329	12.522	13.717	14.906	16.087	17.259	—
52°	9.020	10.172	11.352	12.546	13.741	14.930	16.111	17.282	—
54°	9.043	10.195	11.376	12.570	13.765	14.953	16.135	17.305	—
56°	9.066	10.219	11.400	12.594	13.788	14.977	16.158	17.329	—
58°	9.088	10.242	11.424	12.618	13.812	15.001	16.182	17.352	—
60°	9.111	10.266	11.448	12.642	13.836	15.024	16.205	17.376	—
62°	9.134	10.289	11.471	12.666	13.860	15.048	16.229	17.399	—
64°	9.157	10.313	11.495	12.690	13.884	15.072	16.252	17.422	—
66°	9.180	10.336	11.519	12.714	13.907	15.096	16.276	17.445	—
68°	9.202	10.359	11.543	12.738	13.931	15.119	16.299	17.468	—
70°	9.225	10.383	11.567	12.762	13.955	15.143	16.322	17.492	—
72°	9.248	10.406	11.590	12.785	13.979	15.167	16.346	17.515	—
74°	9.271	10.430	11.614	12.809	14.003	15.190	16.369	17.538	—
76°	9.294	10.453	11.638	12.833	14.026	15.214	16.393	17.562	—
78°	9.317	10.476	11.662	12.857	14.050	15.237	16.416	17.585	—
80°	9.340	10.500	11.686	12.881	14.074	15.261	16.440	17.608	—
82°	9.362	10.524	11.709	12.905	14.098	15.285	16.463	17.631	—
84°	9.385	10.547	11.733	12.929	14.122	15.308	16.487	17.655	—
86°	9.408	10.571	11.757	12.953	14.145	15.332	16.510	17.678	—
88°	9.431	10.594	11.781	12.977	14.169	15.356	16.533	17.701	—
90°	9.454	10.618	11.805	13.000	14.193	15.379	16.557	17.724	—
92°	9.477	10.641	11.828	13.024	14.217	15.403	16.580	17.748	—
94°	9.500	10.665	11.852	13.048	14.241	15.427	16.604	17.771	—
96°	9.523	10.689	11.876	13.072	14.264	15.450	16.627	17.794	—
98°	9.546	10.712	11.900	13.096	14.288	15.474	16.651	17.817	—
100°	9.569	10.736	11.924	13.120	14.312	15.498	16.674	17.841	—
M. V. per °C.	.0114	.0117	.0119	.0120	.0119	.0119	.0118	.0117	.0116

TABLE V  
PLAT. VS. PLAT. + 10% RHODIUM THERMOCOUPLE<sup>1</sup>  
Degrees Fahrenheit, Reference Junction 32°F.

Deg. F.	0°	100°	200°	300°	400°	500°	600°	700°
	Millivolts							
0°	-.0920	.221	.595	1.016	1.473	1.956	2.457	2.975
5°	-.0778	.239	.615	1.038	1.497	1.980	2.482	3.001
10°	-.0636	.257	.635	1.060	1.521	2.005	2.508	3.028
15°	-.0494	.274	.655	1.082	1.544	2.030	2.534	3.054
20°	-.0351	.292	.676	1.105	1.568	2.055	2.560	3.081
25°	-.0207	.310	.696	1.127	1.592	2.080	2.585	3.107
30°	-.0060	.328	.717	1.150	1.616	2.105	2.611	3.133
35°	+.0090	.346	.737	1.173	1.640	2.130	2.637	3.159
40°	.0243	.365	.758	1.196	1.664	2.155	2.663	3.186
45°	.0398	.383	.779	1.218	1.688	2.180	2.689	3.212
50°	.0555	.401	.800	1.241	1.712	2.205	2.715	3.239
55°	.0714	.420	.821	1.264	1.736	2.230	2.741	3.266
60°	.0875	.439	.843	1.287	1.760	2.255	2.767	3.293
65°	.104	.458	.864	1.310	1.784	2.280	2.793	3.319
70°	.120	.477	.886	1.333	1.808	2.305	2.819	3.346
75°	.137	.496	.907	1.356	1.832	2.330	2.845	3.372
80°	.153	.516	.929	1.380	1.857	2.356	2.871	3.399
85°	.170	.535	.950	1.403	1.881	2.381	2.897	3.425
90°	.187	.555	.972	1.426	1.906	2.406	2.923	3.452
95°	.204	.575	.994	1.449	1.931	2.431	2.949	3.478
100°	.221	.595	1.016	1.473	1.956	2.457	2.975	3.505
M.V. per °F.	.00313	.00374	.00421	.00457	.00483	.00501	.00518	.00530

Deg. F.	800°	900°	1000°	1100°	1200°	1300°	1400°	1500°
	Millivolts							
0°	3.505	4.044	4.594	5.155	5.725	6.307	6.898	7.500
5°	3.532	4.071	4.621	5.183	5.754	6.336	6.928	7.530
10°	3.559	4.098	4.649	5.211	5.783	6.366	6.958	7.561
15°	3.585	4.125	4.677	5.239	5.812	6.395	6.987	7.591
20°	3.612	4.153	4.705	5.268	5.841	6.424	7.017	7.621
25°	3.639	4.180	4.733	5.296	5.869	6.453	7.047	7.651
30°	3.667	4.208	4.761	5.324	5.898	6.483	7.077	7.682
35°	3.694	4.235	4.789	5.352	5.927	6.512	7.107	7.713
40°	3.720	4.263	4.817	5.381	5.956	6.542	7.137	7.744
45°	3.747	4.290	4.845	5.409	5.985	6.571	7.167	7.774
50°	3.774	4.318	4.873	5.438	6.015	6.601	7.198	7.805
55°	3.801	4.345	4.901	5.466	6.044	6.630	7.228	7.835
60°	3.828	4.373	4.929	5.495	6.073	6.660	7.258	7.866
65°	3.855	4.400	4.957	5.524	6.102	6.690	7.288	7.897
70°	3.882	4.428	4.985	5.553	6.132	6.720	7.318	7.928
75°	3.909	4.455	5.013	5.581	6.161	6.749	7.348	7.958
80°	3.936	4.483	5.042	5.610	6.190	6.779	7.379	7.989
85°	3.963	4.511	5.070	5.638	6.219	6.808	7.409	8.020
90°	3.990	4.539	5.098	5.667	6.249	6.838	7.439	8.051
95°	4.017	4.566	5.126	5.696	6.278	6.868	7.469	8.081
100°	4.044	4.594	5.155	5.725	6.307	6.898	7.500	8.112
M.V. per °F.	.00539	.00550	.00561	.00570	.00582	.00591	.00602	.00612

<sup>1</sup>Leeds & Northrup Std. 21031.See also W. F. Roeser and H. T. Wensel, *Bur. Standards J. Research*, 10, 275 (1933).

TABLE V.—(Continued)

Deg. F.	1600°	1700°	1800°	1900°	2000°	2100°	2200°	2300°
	Millivolts							
0°	8.112	8.734	9.365	10.007	10.657	11.316	11.977	12.642
5°	8.143	8.765	9.397	10.039	10.690	11.349	12.010	12.675
10°	8.174	8.796	9.429	10.071	10.723	11.382	12.043	12.708
15°	8.205	8.827	9.461	10.103	10.756	11.415	12.076	12.741
20°	8.236	8.859	9.493	10.136	10.789	11.448	12.110	12.775
25°	8.267	8.890	9.525	10.168	10.822	11.481	12.143	12.808
30°	8.298	8.922	9.557	10.201	10.855	11.514	12.177	12.841
35°	8.329	8.953	9.589	10.233	10.887	11.547	12.210	12.874
40°	8.360	8.985	9.621	10.266	10.920	11.580	12.243	12.907
45°	8.391	9.016	9.653	10.298	10.953	11.613	12.276	12.941
50°	8.422	9.048	9.685	10.331	10.986	11.646	12.310	12.974
55°	8.453	9.079	9.717	10.363	11.019	11.679	12.343	13.007
60°	8.484	9.111	9.749	10.396	11.052	11.712	12.376	13.040
65°	8.515	9.143	9.781	10.428	11.085	11.745	12.409	13.074
70°	8.546	9.175	9.813	10.461	11.118	11.778	12.442	13.107
75°	8.577	9.206	9.845	10.493	11.151	11.811	12.475	13.140
80°	8.609	9.238	9.877	10.526	11.184	11.844	12.509	13.173
85°	8.640	9.270	9.909	10.558	11.217	11.877	12.542	13.206
90°	8.671	9.302	9.942	10.591	11.250	11.911	12.575	13.239
95°	8.702	9.333	9.974	10.624	11.283	11.944	12.608	13.272
100°	8.734	9.365	10.007	10.657	11.316	11.977	12.642	13.305
M.V. per °F.	.00622	.00631	.00642	.00650	.00659	.00661	.00665	.00668

Deg. F.	2400°	2500°	2600°	2700°	2800°	2900°	3000°	3100°
	Millivolts							
0°	13.305	13.968	14.629	15.288	15.943	16.596	17.247	17.892
5°	13.339	14.001	14.662	15.321	15.976	16.629	17.279	17.925
10°	13.372	14.034	14.695	15.353	16.009	16.661	17.311	17.957
15°	13.405	14.067	14.728	15.386	16.042	16.694	17.344	17.989
20°	13.438	14.100	14.761	15.418	16.074	16.726	17.376	18.021
25°	13.472	14.133	14.794	15.451	16.107	16.759	17.408	—
30°	13.505	14.166	14.826	15.484	16.139	16.791	17.440	—
35°	13.538	14.200	14.859	15.517	16.172	16.824	17.473	—
40°	13.571	14.233	14.892	15.550	16.205	16.856	17.505	—
45°	13.604	14.266	14.925	15.583	16.238	16.889	17.538	—
50°	13.637	14.299	14.958	15.615	16.270	16.922	17.570	—
55°	13.670	14.332	14.991	15.648	16.303	16.955	17.602	—
60°	13.703	14.365	15.024	15.680	16.335	16.987	17.634	—
65°	13.737	14.398	15.057	15.713	16.368	17.020	17.667	—
70°	13.770	14.431	15.090	15.746	16.401	17.052	17.699	—
75°	13.803	14.464	15.123	15.779	16.434	17.085	17.731	—
80°	13.836	14.497	15.156	15.812	16.466	17.117	17.763	—
85°	13.869	14.530	15.189	15.845	16.499	17.150	17.796	—
90°	13.902	14.563	15.222	15.878	16.531	17.182	17.828	—
95	13.935	14.596	15.255	15.911	16.564	17.215	17.860	—
100°	13.968	14.629	15.288	15.943	16.596	17.247	17.892	—
M.V. per °F.	.00663	.00661	.00659	.00655	.00653	.00651	.00645	.00645

TABLE VI  
PLAT. VS. PLAT. + 13% RHODIUM THERMOCOUPLE<sup>1</sup>  
Degrees Centigrade, Reference Junction 0°C.

Deg. C.	0°	100°	200°	300°	400°	500°	600°	700°	800°
	Millivolts								
0	0.000	.646	1.464	2.394	3.398	4.454	5.561	6.720	7.927
2	.011	.661	1.482	2.414	3.419	4.476	5.583	6.743	7.951
4	.022	.676	1.500	2.433	3.439	4.497	5.606	6.767	7.976
6	.033	.691	1.518	2.453	3.460	4.519	5.629	6.791	8.000
8	.044	.706	1.536	2.472	3.480	4.540	5.652	6.815	8.025
10	.056	.721	1.553	2.492	3.501	4.562	5.675	6.839	8.049
12	.067	.736	1.570	2.512	3.521	4.583	5.698	6.862	8.073
14	.079	.752	1.588	2.531	3.542	4.605	5.721	6.886	8.098
16	.090	.767	1.606	2.551	3.563	4.627	5.744	6.910	8.123
18	.102	.783	1.624	2.570	3.584	4.649	5.767	6.934	8.148
20	.113	.798	1.642	2.590	3.605	4.671	5.790	6.958	8.173
22	.125	.813	1.660	2.609	3.626	4.693	5.813	6.981	8.198
24	.137	.829	1.678	2.629	3.647	4.715	5.836	7.005	8.222
26	.149	.845	1.696	2.649	3.668	4.737	5.859	7.029	8.247
28	.161	.861	1.714	2.669	3.689	4.759	5.882	7.053	8.271
30	.173	.877	1.733	2.689	3.711	4.781	5.905	7.077	8.296
32	.185	.893	1.751	2.709	3.732	4.803	5.928	7.100	8.321
34	.197	.909	1.770	2.729	3.753	4.825	5.951	7.124	8.346
36	.209	.925	1.788	2.749	3.774	4.847	5.974	7.148	8.371
38	.221	.941	1.807	2.769	3.795	4.869	5.997	7.172	8.396
40	.234	.957	1.825	2.789	3.816	4.891	6.020	7.196	8.421
42	.247	.973	1.844	2.809	3.837	4.913	6.043	7.220	8.446
44	.259	.990	1.862	2.829	3.858	4.935	6.066	7.244	8.471
46	.272	1.006	1.881	2.849	3.879	4.957	6.089	7.268	8.496
48	.284	1.023	1.899	2.869	3.900	4.979	6.112	7.292	8.521
50	.297	1.039	1.918	2.889	3.921	5.002	6.135	7.317	8.546
52	.310	1.055	1.937	2.909	3.942	5.024	6.158	7.341	8.571
54	.324	1.072	1.955	2.929	3.963	5.046	6.181	7.365	8.596
56	.337	1.088	1.974	2.949	3.984	5.068	6.204	7.389	8.621
58	.351	1.105	1.992	2.969	4.005	5.090	6.227	7.413	8.646
60	.364	1.121	2.011	2.990	4.027	5.113	6.251	7.438	8.671
62	.377	1.138	2.030	3.010	4.048	5.135	6.274	7.462	8.696
64	.391	1.154	2.049	3.030	4.069	5.157	6.298	7.487	8.721
66	.404	1.171	2.068	3.050	4.090	5.179	6.321	7.511	8.746
68	.418	1.187	2.087	3.070	4.111	5.201	6.345	7.536	8.771
70	.431	1.204	2.106	3.091	4.133	5.224	6.368	7.560	8.796
72	.444	1.221	2.125	3.111	4.154	5.246	6.391	7.584	8.821
74	.458	1.238	2.144	3.132	4.175	5.269	6.415	7.609	8.847
76	.472	1.255	2.163	3.152	4.196	5.291	6.438	7.633	8.872
78	.486	1.272	2.182	3.173	4.217	5.314	6.462	7.658	8.898
80	.500	1.290	2.201	3.193	4.239	5.336	6.485	7.682	8.923
82	.514	1.307	2.220	3.213	4.260	5.358	6.508	7.706	8.948
84	.529	1.324	2.239	3.234	4.282	5.381	6.532	7.731	8.973
86	.543	1.341	2.258	3.254	4.303	5.403	6.555	7.755	8.998
88	.558	1.358	2.277	3.275	4.325	5.426	6.579	7.780	9.023
90	.572	1.376	2.297	3.295	4.346	5.448	6.602	7.804	9.049
92	.587	1.394	2.316	3.316	4.368	5.471	6.626	7.829	9.075
94	.602	1.411	2.336	3.336	4.389	5.493	6.649	7.853	9.100
96	.617	1.429	2.355	3.357	4.411	5.516	6.673	7.878	9.126
98	.632	1.446	2.375	3.377	4.432	5.538	6.696	7.902	9.151
100	.646	1.464	2.394	3.398	4.454	5.561	6.720	7.927	9.177
M.V. per °C.	.00646	.00818	.00930	.01004	.01056	.01107	.01159	.01207	.01250

<sup>1</sup> Leeds & Northrup Std. 21031.See also W. F. Roeser and H. T. Wensel, *Bur. Standards J. Research*, 10, 275 (1938).

TABLE VI.—(Continued)

Deg. C.	900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°	
	Millivolts								
0	9.177	10.470	11.811	13.181	14.563	15.940	17.316	18.680	—
2	9.202	10.496	11.838	13.208	14.591	15.968	17.343	18.707	—
4	9.228	10.522	11.865	13.236	14.618	15.995	17.371	18.734	—
6	9.253	10.548	11.892	13.263	14.646	16.023	17.398	18.761	—
8	9.279	10.574	11.919	13.291	14.673	16.050	17.426	18.788	—
10	9.304	10.601	11.947	13.318	14.701	16.078	17.453	18.815	—
12	9.330	10.627	11.974	13.346	14.728	16.105	17.480	18.842	—
14	9.355	10.654	12.002	13.373	14.756	16.133	17.508	18.869	—
16	9.381	10.680	12.029	13.401	14.783	16.160	17.535	18.896	—
18	9.406	10.707	12.057	13.428	14.811	16.188	17.563	18.923	—
20	9.432	10.733	12.084	13.456	14.838	16.215	17.590	18.951	—
22	9.458	10.759	12.111	13.483	14.865	16.242	17.617	18.978	—
24	9.483	10.786	12.138	13.511	14.893	16.270	17.645	19.005	—
26	9.509	10.813	12.165	13.539	14.920	16.298	17.672	19.032	—
28	9.534	10.840	12.192	13.567	14.948	16.326	17.700	19.059	—
30	9.560	10.867	12.219	13.595	14.975	16.354	17.727	19.087	—
32	9.585	10.894	12.246	13.623	15.002	16.381	17.754	19.114	—
34	9.611	10.920	12.274	13.650	15.030	16.409	17.782	19.141	—
36	9.637	10.947	12.301	13.678	15.058	16.437	17.809	19.168	—
38	9.663	10.973	12.329	13.705	15.086	16.465	17.837	19.195	—
40	9.689	11.000	12.356	13.733	15.114	16.493	17.864	19.222	—
42	9.715	11.027	12.383	13.761	15.142	16.521	17.891	19.249	—
44	9.740	11.054	12.411	13.788	15.169	16.548	17.918	19.276	—
46	9.766	11.081	12.438	13.816	15.197	16.576	17.945	19.303	—
48	9.791	11.108	12.466	13.843	15.224	16.603	17.972	19.330	—
50	9.817	11.135	12.493	13.871	15.252	16.631	18.000	19.357	—
52	9.843	11.161	12.520	13.898	15.279	16.659	18.027	19.384	—
54	9.869	11.188	12.548	13.926	15.307	16.686	18.054	19.411	—
56	9.895	11.215	12.575	13.954	15.334	16.714	18.081	19.438	—
58	9.921	11.242	12.603	13.982	15.362	16.741	18.108	19.465	—
60	9.947	11.269	12.630	14.010	15.389	16.769	18.135	19.492	—
62	9.973	11.296	12.658	14.037	15.417	16.796	18.162	19.519	—
64	9.999	11.323	12.685	14.065	15.444	16.824	18.189	19.546	—
66	10.025	11.350	12.713	14.092	15.472	16.851	18.216	19.573	—
68	10.051	11.377	12.740	14.120	15.499	16.879	18.243	19.600	—
70	10.078	11.404	12.768	14.147	15.527	16.906	18.271	19.627	—
72	10.104	11.431	12.796	14.175	15.554	16.933	18.298	19.654	—
74	10.130	11.458	12.823	14.202	15.582	16.961	18.325	19.681	—
76	10.156	11.485	12.851	14.230	15.609	16.988	18.352	19.708	—
78	10.182	11.512	12.878	14.257	15.637	17.016	18.379	19.735	—
80	10.208	11.540	12.906	14.285	15.664	17.043	18.407	19.762	—
82	10.234	11.567	12.933	14.312	15.691	17.070	18.434	19.789	—
84	10.260	11.594	12.961	14.340	15.719	17.098	18.461	19.816	—
86	10.286	11.621	12.988	14.368	15.747	17.125	18.488	19.843	—
88	10.312	11.648	13.016	14.396	15.775	17.153	18.515	19.870	—
90	10.339	11.676	13.043	14.424	15.803	17.180	18.543	19.897	—
92	10.365	11.703	13.071	14.451	15.830	17.207	18.570	19.924	—
94	10.391	11.730	13.098	14.479	15.858	17.234	18.598	19.951	—
96	10.417	11.757	13.126	14.507	15.885	17.261	18.625	19.978	—
98	10.443	11.784	13.153	14.535	15.913	17.288	18.653	20.005	—
100	10.470	11.811	13.181	14.563	15.940	17.316	18.680	20.032	—
M.V. per °C.	.01203	.01341	.01370	.01382	.01377	.01376	.01364	.01352	—

TABLE VII  
PLAT. VS. PLAT. + 13% RHODIUM THERMOCOUPLE<sup>1</sup>  
Degrees Fahrenheit, Reference Junction 32°F.

Deg. F.	0°	100°	200°	300°	400°	500°	600°	700°
	Millivolts							
0	-.0890	.220	.596	1.030	1.504	2.012	2.546	3.102
5	-.0756	.237	.617	1.052	1.528	2.038	2.574	3.131
10	-.0621	.255	.637	1.075	1.553	2.064	2.601	3.159
15	-.0484	.272	.658	1.098	1.578	2.090	2.629	3.187
20	-.0346	.290	.679	1.121	1.603	2.117	2.656	3.216
25	-.0205	.308	.700	1.144	1.628	2.143	2.684	3.244
30	-.0060	.326	.721	1.168	1.653	2.169	2.711	3.272
35	+.0090	.344	.742	1.191	1.678	2.196	2.739	3.301
40	.0244	.363	.764	1.214	1.703	2.225	2.766	3.329
45	.0399	.381	.785	1.238	1.728	2.249	2.794	3.358
50	.0555	.400	.807	1.262	1.754	2.276	2.822	3.387
55	.0712	.419	.829	1.285	1.779	2.303	2.850	3.415
60	.0871	.438	.851	1.309	1.805	2.330	2.878	3.444
65	.103	.457	.873	1.333	1.830	2.357	2.906	3.473
70	.119	.477	.895	1.357	1.856	2.384	2.934	3.501
75	.136	.496	.917	1.381	1.882	2.411	2.962	3.530
80	.152	.516	.939	1.406	1.908	2.438	2.990	3.559
85	.169	.536	.962	1.430	1.933	2.465	3.018	3.588
90	.186	.556	.984	1.454	1.959	2.492	3.046	3.617
95	.203	.576	1.007	1.479	1.985	2.519	3.074	3.646
100	.220	.596	1.030	1.504	2.012	2.546	3.102	3.675
M.V. per °F.	.00131	.00376	.00434	.00474	.00508	.00534	.00556	.00573

Deg. F.	800°	900°	1000°	1100°	1200°	1300°	1400°	1500°
	Millivolts							
0	3.675	4.263	4.867	5.486	6.122	6.773	7.438	8.118
5	3.704	4.293	4.898	5.517	6.155	6.806	7.471	8.152
10	3.733	4.323	4.928	5.548	6.187	6.839	7.505	8.187
15	3.763	4.353	4.959	5.580	6.219	6.872	7.539	8.221
20	3.792	4.382	4.990	5.611	6.251	6.905	7.573	8.255
25	3.821	4.412	5.021	5.643	6.284	6.938	7.606	8.290
30	3.850	4.442	5.051	5.675	6.316	6.971	7.640	8.324
35	3.880	4.472	5.082	5.706	6.348	7.004	7.674	8.359
40	3.909	4.502	5.113	5.738	6.381	7.037	7.708	8.393
45	3.938	4.532	5.144	5.770	6.413	7.071	7.742	8.428
50	3.968	4.562	5.175	5.802	6.446	7.104	7.776	8.463
55	3.997	4.593	5.206	5.834	6.478	7.137	7.810	8.497
60	4.027	4.623	5.237	5.866	6.511	7.170	7.844	8.532
65	4.056	4.653	5.268	5.898	6.544	7.204	7.878	8.567
70	4.086	4.684	5.299	5.930	6.576	7.237	7.912	8.601
75	4.115	4.714	5.330	5.962	6.609	7.270	7.947	8.636
80	4.145	4.745	5.361	5.994	6.642	7.304	7.981	8.671
85	4.174	4.775	5.392	6.026	6.675	7.337	8.015	8.706
90	4.204	4.806	5.423	6.058	6.707	7.371	8.049	8.741
95	4.234	4.836	5.454	6.090	6.740	7.404	8.084	8.776
100	4.263	4.867	5.486	6.122	6.773	7.438	8.118	8.811
M.V. per °F.	.00588	.00604	.00619	.00636	.00651	.00666	.00680	.00693

<sup>1</sup> Leeds & Northrup Std. 21031.See also W. F. Roeser and H. T. Wensel, *Bur. Standards J. Research*, **10**, 275 (1933).

TABLE VII.—(Continued)

Deg. F.	1600°	1700°	1800°	1900°	2000°	2100°	2200°	2300°
	Millivolts							
0	8.811	9.518	10.237	10.970	11.720	12.478	13.242	14.010
5	8.846	9.553	10.274	11.008	11.758	12.516	13.280	14.048
10	8.881	9.589	10.310	11.045	11.796	12.554	13.319	14.087
15	8.916	9.625	10.346	11.082	11.834	12.592	13.357	14.125
20	8.951	9.661	10.383	11.119	11.871	12.630	13.396	14.164
25	8.986	9.696	10.419	11.157	11.909	12.668	13.434	14.202
30	9.021	9.732	10.455	11.194	11.947	12.707	13.472	14.240
35	9.056	9.768	10.492	11.231	11.985	12.745	13.511	14.279
40	9.092	9.804	10.528	11.269	12.023	12.783	13.549	14.317
45	9.127	9.840	10.565	11.306	12.061	12.821	13.588	14.355
50	9.162	9.876	10.602	11.344	12.098	12.859	13.626	14.394
55	9.198	9.912	10.638	11.381	12.136	12.898	13.664	14.432
60	9.233	9.948	10.675	11.419	12.174	12.936	13.703	14.470
65	9.269	9.984	10.712	11.457	12.212	12.974	13.741	14.509
70	9.304	10.020	10.749	11.494	12.250	13.012	13.780	14.547
75	9.340	10.056	10.786	11.532	12.288	13.051	13.818	14.585
80	9.375	10.092	10.822	11.569	12.326	13.089	13.856	14.624
85	9.411	10.129	10.859	11.607	12.364	13.127	13.895	14.662
90	9.446	10.165	10.896	11.645	12.402	13.165	13.933	14.700
95	9.482	10.201	10.933	11.683	12.440	13.204	13.972	14.739
100	9.518	10.237	10.970	11.720	12.478	13.242	14.010	14.777
M.V. per °F.	.00707	.00719	.00733	.00750	.00758	.00764	.00768	.00767

Deg. F.	2400°	2500°	2600°	2700°	2800°	2900°	3000°
	Millivolts						
0	14.777	15.543	16.309	17.073	17.833	18.588	19.342
5	14.815	15.581	16.347	17.111	17.871	18.626	19.379
10	14.854	15.619	16.385	17.149	17.909	18.663	19.417
15	14.892	15.658	16.423	17.187	17.947	18.701	19.455
20	14.930	15.696	16.462	17.225	17.985	18.739	19.492
25	14.969	15.734	16.500	17.263	18.022	18.777	19.530
30	15.007	15.773	16.538	17.302	18.060	18.814	19.567
35	15.045	15.811	16.576	17.340	18.098	18.852	19.605
40	15.084	15.849	16.614	17.378	18.136	18.890	19.642
45	15.122	15.887	16.653	17.416	18.173	18.927	19.680
50	15.160	15.926	16.691	17.454	18.211	18.965	19.717
55	15.198	15.964	16.729	17.492	18.249	19.003	19.755
60	15.237	16.002	16.767	17.530	18.286	19.040	19.793
65	15.275	16.041	16.805	17.568	18.324	19.078	19.830
70	15.313	16.079	16.844	17.606	18.362	19.116	19.868
75	15.352	16.117	16.882	17.643	18.400	19.154	19.905
80	15.390	16.156	16.920	17.682	18.437	19.191	19.943
85	15.428	16.194	16.958	17.720	18.475	19.229	19.980
90	15.466	16.232	16.996	17.758	18.513	19.267	20.018
95	15.505	16.270	17.035	17.795	18.550	19.304	20.055
100	15.543	16.309	17.073	17.833	18.588	19.342	20.093
M.V. per °F.	.00766	.00766	.00764	.00760	.00755	.00755	.00751



TABLE VIII  
CHROMEL VS. ALUMEL THERMOCOUPLE<sup>1</sup>  
Degrees Centigrade, Reference Junction 0°C.

Deg. C.	-100°	-0°	0°	100°	200°	300°	400°	500°
	Millivolts							
0°	-3.49	0	0	4.10	8.13	12.21	16.39	20.64
2°	-3.55	-.08	.08	4.18	8.21	12.29	16.47	20.73
4°	-3.60	-.16	.16	4.26	8.29	12.37	16.55	20.81
6°	-3.66	-.23	.24	4.34	8.37	12.45	16.64	20.90
8°	-3.72	-.31	.32	4.42	8.45	12.53	16.73	20.98
10°	-3.78	-.39	.40	4.51	8.53	12.62	16.82	21.07
12°	-3.83	-.47	.48	4.59	8.61	12.70	16.90	21.15
14°	-3.89	-.54	.56	4.67	8.69	12.78	16.99	21.24
16°	-3.94	-.62	.64	4.75	8.77	12.86	17.07	21.32
18°	-4.00	-.69	.72	4.83	8.85	12.95	17.16	21.41
20°	-4.05	-.77	.80	4.92	8.93	13.04	17.24	21.49
22°	-4.10	-.84	.88	5.00	9.01	13.12	17.32	21.58
24°	-4.16	-.92	.96	5.08	9.09	13.20	17.41	21.66
26°	-4.21	-.99	1.04	5.16	9.17	13.28	17.49	21.75
28°	-4.27	-1.07	1.12	5.24	9.25	13.36	17.58	21.83
30°	-4.32	-1.14	1.20	5.33	9.34	13.45	17.66	21.92
32°	-4.37	-1.21	1.28	5.41	9.42	13.53	17.74	22.00
34°	-4.42	-1.28	1.36	5.49	9.50	13.61	17.83	22.09
36°	-4.47	-1.36	1.44	5.57	9.58	13.69	17.91	22.17
38°	-4.52	-1.43	1.52	5.65	9.66	13.78	18.00	22.26
40°	-4.57	-1.50	1.61	5.73	9.74	13.87	18.08	22.34
42°	-4.62	-1.57	1.69	5.81	9.82	13.95	18.16	22.43
44°	-4.67	-1.64	1.77	5.89	9.90	14.03	18.25	22.52
46°	-4.71	-1.72	1.85	5.97	9.98	14.11	18.33	22.60
48°	-4.76	-1.79	1.93	6.05	10.06	14.20	18.42	22.68
50°	-4.81	-1.86	2.02	6.13	10.15	14.29	18.50	22.77
52°	-4.85	-1.95	2.10	6.21	10.23	14.37	18.58	22.86
54°	-4.90	-2.00	2.18	6.29	10.31	14.45	18.66	22.94
56°	-4.94	-2.07	2.26	6.37	10.39	14.53	18.75	23.03
58°	-4.99	-2.14	2.34	6.45	10.47	14.62	18.84	23.11
60°	-5.03	-2.21	2.43	6.53	10.56	14.71	18.93	23.20
62°	-5.07	-2.28	2.51	6.61	10.64	14.79	19.02	23.28
64°	-5.11	-2.35	2.59	6.69	10.72	14.88	19.11	23.37
66°	-5.16	-2.41	2.67	6.77	10.80	14.96	19.20	23.45
68°	-5.20	-2.48	2.76	6.85	10.88	15.05	19.28	23.54
70°	-5.24	-2.55	2.85	6.93	10.97	15.13	19.36	23.62
72°	-5.28	-2.61	2.93	7.01	11.05	15.21	19.44	23.71
74°	-5.32	-2.68	3.01	7.09	11.13	15.30	19.53	23.79
76°	-5.35	-2.74	3.09	7.17	11.21	15.38	19.61	23.88
78°	-5.39	-2.81	3.17	7.25	11.29	15.47	19.70	23.96
80°	-5.43	-2.87	3.26	7.33	11.38	15.55	19.78	24.05
82°	-5.46	-2.93	3.34	7.41	11.46	15.63	19.87	24.14
84°	-5.50	-3.00	3.42	7.49	11.54	15.72	19.95	24.22
86°	-5.53	-3.06	3.50	7.57	11.62	15.80	20.04	24.31
88°	-5.57	-3.13	3.59	7.65	11.71	15.89	20.12	24.39
90°	-5.60	-3.19	3.68	7.73	11.80	15.97	20.21	24.48
92°	-5.63	-3.25	3.76	7.81	11.88	16.05	20.30	24.56
94°	-5.66	-3.31	3.84	7.89	11.96	16.14	20.38	24.65
96°	-5.69	-3.37	3.92	7.97	12.04	16.22	20.47	24.73
98°	-5.72	-3.43	4.01	8.05	12.12	16.31	20.55	24.82
100°	-5.75	-3.49	4.10	8.13	12.21	16.39	20.64	24.90
M.V. per °C.			.041	.0403	.0408	.0413	.0425	.0426

<sup>1</sup> Leeds & Northrup Std. 21031 (values above 0°C).See also W. F. Roeser, A. I. Dahl and G. J. Gowen, *J. Research Nat. Bur. Standards* 44 990

TABLE VIII.—(Continued)

Deg. C.	600°	700°	800°	900°	1000°	1100°	1200°	1300°
	Millivolts							
0°	24.90	29.14	33.31	37.36	41.31	45.14	48.85	52.41
2°	24.99	29.22	33.39	37.44	41.39	45.22	48.93	52.48
4°	25.07	29.31	33.47	37.52	41.47	45.29	49.00	52.55
6°	25.16	29.39	33.55	37.60	41.55	45.37	49.07	52.62
8°	25.24	29.48	33.63	37.68	41.63	45.44	49.14	52.69
10°	25.33	29.56	33.71	37.76	41.70	45.52	49.21	52.75
12°	25.41	29.64	33.79	37.84	41.78	45.59	49.29	52.82
14°	25.50	29.73	33.87	37.92	41.86	45.67	49.36	52.89
16°	25.58	29.81	33.95	38.00	41.94	45.74	49.43	52.96
18°	25.67	29.90	34.03	38.08	42.01	45.82	49.50	53.03
20°	25.75	29.98	34.12	38.16	42.08	45.89	49.57	53.10
22°	25.84	30.06	34.20	38.24	42.16	45.97	49.65	53.17
24°	25.93	30.15	34.28	38.32	42.24	46.04	49.73	53.24
26°	26.01	30.23	34.36	38.40	42.32	46.12	49.80	53.31
28°	26.09	30.32	34.44	38.48	42.40	46.19	49.87	53.38
30°	26.18	30.40	34.53	38.56	42.47	46.27	49.94	53.45
32°	26.26	30.48	34.61	38.64	42.55	46.35	50.01	53.52
34°	26.35	30.57	34.69	38.72	42.62	46.43	50.08	53.59
36°	26.43	30.65	34.77	38.80	42.70	46.50	50.15	53.66
38°	26.52	30.74	34.85	38.88	42.78	46.57	50.22	53.73
40°	26.60	30.82	34.94	38.96	42.86	46.64	50.29	53.79
42°	26.69	30.90	35.02	39.04	42.94	46.71	50.37	53.86
44°	26.77	30.98	35.10	39.12	43.02	46.79	50.44	53.93
46°	26.86	31.06	35.18	39.20	43.10	46.86	50.51	54.00
48°	26.94	31.14	35.26	39.28	43.17	46.94	50.58	54.07
50°	27.03	31.23	35.35	39.35	43.24	47.01	50.65	54.13
52°	27.12	31.31	35.43	39.43	43.32	47.08	50.72	54.20
54°	27.20	31.40	35.51	39.51	43.39	47.16	50.79	54.27
56°	27.28	31.48	35.59	39.59	43.47	47.23	50.86	54.34
58°	27.37	31.57	35.67	39.67	43.54	47.31	50.93	54.41
60°	27.45	31.65	35.75	39.75	43.62	47.38	51.00	54.47
62°	27.53	31.73	35.83	39.83	43.70	47.45	51.08	54.54
64°	27.62	31.82	35.91	39.91	43.77	47.53	51.15	54.61
66°	27.70	31.90	35.99	39.99	43.85	47.60	51.22	54.68
68°	27.79	31.99	36.07	40.07	43.92	47.68	51.29	54.75
70°	27.87	32.07	36.16	40.14	44.00	47.75	51.36	54.81
72°	27.95	32.15	36.24	40.22	44.08	47.82	51.43	54.88
74°	28.04	32.23	36.32	40.30	44.15	47.90	51.50	54.95
76°	28.12	32.31	36.40	40.38	44.23	47.97	51.57	55.02
78°	28.21	32.39	36.48	40.46	44.30	48.05	51.64	55.09
80°	28.29	32.48	36.56	40.53	44.38	48.12	51.71	55.15
82°	28.38	32.56	36.64	40.61	44.46	48.20	51.78	55.22
84°	28.46	32.65	36.72	40.69	44.53	48.27	51.85	55.29
86°	28.55	32.73	36.80	40.77	44.61	48.34	51.92	55.36
88°	28.63	32.82	36.88	40.85	44.68	48.41	51.99	55.42
90°	28.72	32.90	36.96	40.92	44.76	48.48	52.06	55.48
92°	28.80	32.98	37.04	41.00	44.84	48.56	52.13	55.55
94°	28.89	33.06	37.12	41.08	44.91	48.64	52.20	55.62
96°	28.97	33.14	37.20	41.16	44.99	48.71	52.27	55.69
98°	29.06	33.22	37.28	41.24	45.06	48.78	52.34	55.75
100°	29.14	33.31	37.36	41.31	45.14	48.85	52.41	55.81
M.V. per °C.	0.424	.0417	.0405	.0395	.0383	.0371	.0356	.0340

TABLE IX  
CHROMEL VS. ALUMEL THERMOCOUPLE<sup>1</sup>  
Degrees Fahrenheit, Reference Junction 32°F.

Deg. F.	-200°	-100°	-0°	0°	100°	200°	300°
	Millivolts						
0°	-4.20	-2.65	-0.68	-0.68	1.52	3.82	6.09
5°	-4.36	-2.74	-.78	-.58	1.63	3.93	6.20
10°	-4.43	-2.83	-.89	-.47	1.74	4.05	6.31
15°	-4.50	-2.92	-.99	-.37	1.85	4.16	6.42
20°	-4.57	-3.01	-1.10	-.26	1.97	4.28	6.53
25°	-4.64	-3.10	-1.20	-.15	2.08	4.39	6.64
30°	-4.71	-3.19	-1.30	-.04	2.20	4.51	6.75
35°	-4.78	-3.27	-1.40	.07	2.31	4.62	6.86
40°	-4.84	-3.36	-1.50	.18	2.43	4.74	6.98
45°	-4.90	-3.44	-1.60	.29	2.54	4.85	7.09
50°	-4.96	-3.52	-1.70	.40	2.66	4.97	7.20
55°	-5.02	-3.60	-1.80	.51	2.77	5.08	7.31
60°	-5.08	-3.68	-1.90	.62	2.89	5.19	7.42
65°	-5.14	-3.76	-2.00	.73	3.00	5.30	7.53
70°	-5.19	-3.84	-2.09	.84	3.12	5.42	7.64
75°	-5.25	-3.92	-2.18	.95	3.24	5.53	7.75
80°	-5.30	-4.00	-2.28	1.06	3.36	5.64	7.87
85°	-5.36	-4.08	-2.37	1.17	3.48	5.75	7.98
90°	-5.41	-4.15	-2.47	1.29	3.59	5.87	8.09
95°	-5.46	-4.22	-2.56	1.40	3.70	5.98	8.20
100°	-5.51	-4.29	-2.65	1.52	3.82	6.09	8.31
M.V. per °F.					.023	.0227	.0222

Deg. F.	400°	500°	600°	700°	800°	900°	1000°
	Millivolts						
0°	8.31	10.56	12.85	15.18	17.52	19.88	22.25
5°	8.42	10.67	12.96	15.29	17.63	20.00	22.37
10°	8.53	10.79	13.08	15.41	17.75	20.12	22.49
15°	8.64	10.90	13.19	15.52	17.87	20.24	22.60
20°	8.76	11.02	13.31	15.64	17.99	20.36	22.72
25°	8.87	11.13	13.43	15.76	18.10	20.47	22.84
30°	8.98	11.25	13.55	15.88	18.22	20.59	22.96
35°	9.09	11.36	13.67	16.00	18.34	20.71	23.08
40°	9.20	11.47	13.78	16.11	18.46	20.83	23.20
45°	9.31	11.58	13.89	16.23	18.58	20.95	23.32
50°	9.43	11.70	14.01	16.35	18.70	21.07	23.43
55°	9.55	11.81	14.12	16.47	18.81	21.18	23.55
60°	9.66	11.93	14.24	16.58	18.93	21.30	23.67
65°	9.77	12.04	14.36	16.70	19.05	21.42	23.79
70°	9.88	12.16	14.48	16.82	19.17	21.54	23.91
75°	9.99	12.27	14.60	16.93	19.29	21.66	24.02
80°	10.11	12.39	14.71	17.05	19.41	21.78	24.14
85°	10.22	12.50	14.83	17.17	19.52	21.89	24.26
90°	10.33	12.62	14.94	17.29	19.64	22.01	24.38
95°	10.44	12.73	15.06	17.40	19.76	22.13	24.50
100°	10.56	12.85	15.18	17.52	19.88	22.25	24.62
M.V. per °F.	.0225	.0229	.0233	.0234	.0236	.0237	.0237

<sup>1</sup> Leeds & Northrup Std. 21031 (values above 0°F).See also W. F. Roeser, A. L. Dahl and G. J. Gowens, *J. Research Nat. Bur. Standards* **14**, 239 (1935).

TABLE IX.—(Continued)

Deg. F.	1100°	1200°	1300°	1400°	1500°	1600°	1700°
	Millivolts						
0°	24.62	26.98	29.33	31.65	33.94	36.20	38.43
5°	24.74	27.10	29.45	31.77	34.06	36.31	38.54
10°	24.85	27.21	29.56	31.88	34.17	36.42	38.65
15°	24.97	27.33	29.68	32.00	34.29	36.54	38.76
20°	25.09	27.45	29.79	32.11	34.40	36.65	38.87
25°	25.21	27.57	29.91	32.23	34.51	36.76	38.98
30°	25.33	27.68	30.02	32.34	34.62	36.87	39.09
35°	25.45	27.80	30.14	32.46	34.74	36.99	39.20
40°	25.57	27.92	30.26	32.57	34.85	37.10	39.31
45°	25.69	28.04	30.38	32.69	34.97	37.21	39.42
50°	25.80	28.15	30.49	32.80	35.08	37.32	39.53
55°	25.92	28.27	30.61	32.92	35.19	37.43	39.64
60°	26.04	28.39	30.72	33.03	35.30	37.54	39.75
65°	26.16	28.51	30.84	33.15	35.42	37.65	39.86
70°	26.27	28.62	30.96	33.26	35.53	37.76	39.96
75°	26.39	28.74	31.08	33.38	35.64	37.88	40.07
80°	26.51	28.86	31.19	33.49	35.75	37.99	40.18
85°	26.63	28.98	31.31	33.60	35.87	38.10	40.29
90°	26.74	29.09	31.42	33.71	35.98	38.21	40.40
95°	26.86	29.21	31.54	33.83	36.09	38.32	40.51
100°	26.98	29.33	31.65	33.94	36.20	38.43	40.62
M.V. per °F.	.0236	.0235	.0232	.0229	.0226	.0223	.0219

Deg. F.	1800°	1900°	2000°	2100°	2200°	2300°	2400°
	Millivolts						
0°	40.62	42.77	44.89	46.97	49.01	51.00	52.95
5°	40.73	42.88	45.00	47.08	49.11	51.10	53.05
10°	40.83	42.98	45.10	47.18	49.21	51.20	53.14
15°	40.94	43.09	45.20	47.28	49.31	51.30	53.24
20°	41.05	43.20	45.31	47.38	49.41	51.39	53.33
25°	41.16	43.31	45.41	47.49	49.51	51.49	53.43
30°	41.27	43.41	45.52	47.59	49.61	51.59	53.52
35°	41.38	43.52	45.62	47.69	49.71	51.69	53.62
40°	41.48	43.62	45.73	47.79	49.81	51.78	53.71
45°	41.59	43.73	45.83	47.89	49.91	51.88	53.81
50°	41.70	43.83	45.93	47.99	50.01	51.98	53.90
55°	41.81	43.94	46.04	48.10	50.11	52.08	54.00
60°	41.91	44.04	46.14	48.20	50.21	52.17	54.09
65°	42.02	44.15	46.25	48.30	50.31	52.27	54.19
70°	42.13	44.26	46.35	48.40	50.41	52.37	54.28
75°	42.24	44.37	46.46	48.51	50.51	52.47	54.38
80°	42.34	44.47	46.56	48.61	50.61	52.56	54.47
85°	42.45	44.58	46.66	48.71	50.71	52.66	54.57
90°	42.56	44.68	46.76	48.81	50.80	52.75	54.66
95°	42.67	44.79	43.87	48.91	50.90	52.85	54.76
100°	42.77	44.89	46.97	49.01	51.00	52.95	54.85
M.V. per °F.	.0215	.0212	.0208	.0204	.0199	.0195	.0190

TABLE X  
COPPER VS. CONSTANTAN THERMOCOUPLE<sup>1</sup>  
Degrees Centigrade, Reference Junction 0°C.

Temperature (°C.)	Electro- motive force (mv.)	Temperature (°C.)	Electro- motive force (mv.)	Temperature (°C.)	Electro- motive force (mv.)
-200	-5.539	0	0.000	200	9.285
-190	-5.378	10	.389	210	9.820
-180	-5.204	20	.787	220	10.360
-170	-5.016	30	1.194	230	10.905
-160	-4.815	40	1.610	240	11.455
-150	-4.602	50	2.034	250	12.010
-140	-4.376	60	2.467	260	12.571
-130	-4.137	70	2.908	270	13.136
-120	-3.886	80	3.356	280	13.706
-110	-3.623	90	3.812	290	14.280
-100	-3.349	100	4.276	300	14.859
-90	-3.063	110	4.747	310	15.443
-80	-2.765	120	5.225	320	16.030
-70	-2.456	130	5.710	330	16.621
-60	-2.137	140	6.202	340	17.216
-50	-1.807	150	6.700	350	17.815
-40	-1.466	160	7.205	360	18.418
-30	-1.114	170	7.716	370	19.025
-20	-0.752	180	8.233	380	19.635
-10	-0.381	190	8.756	390	20.248
0	.000	200	9.285	400	20.865

<sup>1</sup> W. F. Roeser and A. I. Dahl, *J. Research Nat. Bur. Standards*, 20, 337 (1938).

TABLE XI  
COPPER VS. CONSTANTAN THERMOCOUPLE  
Degrees Fahrenheit, Reference Junction 32°F.

Temperature (°F.)	E.m.f. (mv.)	Temperature (°F.)	E.m.f. (mv.)	Temperature (°F.)	E.m.f. (mv.)	Temperature (°F.)	E.m.f. (mv.)
-300	-5.283	0	-0.671	300	6.644	600	15.769
-290	-5.184	10	-.464	310	6.924	610	16.096
-280	-5.081	20	-.255	320	7.206	620	16.424
-270	-4.973	30	-.043	330	7.489	630	16.753
-260	-4.861	40	+.172	340	7.774	640	17.084
-250	-4.745	50	.390	350	8.061	650	17.416
-240	-4.626	60	.610	360	8.350	660	17.749
-230	-4.503	70	.832	370	8.640	670	18.083
-220	-4.376	80	1.057	380	8.932	680	18.418
-210	-4.245	90	1.285	390	9.226	690	18.754
-200	-4.110	100	1.516	400	9.521	700	19.091
-190	-3.971	110	1.750	410	9.819	710	19.430
-180	-3.829	120	1.987	420	10.119	720	19.770
-170	-3.683	130	2.226	430	10.420	730	20.111
-160	-3.533	140	2.467	440	10.722	740	20.453
-150	-3.380	150	2.711	450	11.026	750	20.796
-140	-3.223	160	2.957	460	11.332		
-130	-3.062	170	3.206	470	11.639		
-120	-2.898	180	3.457	480	11.948		
-110	-2.731	190	3.710	490	12.259		
-100	-2.560	200	3.966	500	12.571		
-90	-2.386	210	4.224	510	12.885		
-80	-2.209	220	4.484	520	13.200		
-70	-2.028	230	4.747	530	13.516		
-60	-1.844	240	5.012	540	13.833		
-50	-1.656	250	5.279	550	14.152		
-40	-1.465	260	5.548	560	14.472		
-30	-1.271	270	5.819	570	14.794		
-20	-1.074	280	6.092	580	15.118		
-10	-0.874	290	6.367	590	15.443		
0	-.671	300	6.644	600	15.769		

<sup>1</sup> W. F. Roeser and A. I. Dahl, *J. Research Nat. Bur. Standards*, 20, 337 (1938).

TABLE XII  
IRON VS. CONSTANTAN THERMOCOUPLE<sup>1</sup>  
Degrees Centigrade, Reference Junction 0°C.

Temperature (°C.)	E.m.f. (mv.)	Temperature (°C.)	E.m.f. (mv.)	Temperature (°C.)	E.m.f. (mv.)	Temperature (°C.)	E.m.f. (mv.)
		0	0.00	400	22.07	800	45.72
		10	0.52	410	22.62	810	46.37
		20	1.05	420	23.17	820	47.03
		30	1.58	430	23.72	830	47.69
		40	2.12	440	24.27	840	48.34
		50	2.66	450	24.82	850	49.00
		60	3.20	460	25.37	860	49.66
		70	3.75	470	25.92	870	50.32
		80	4.30	480	26.47	880	50.97
		90	4.85	490	27.03	890	51.63
		100	5.40	500	27.58	900	52.29
		110	5.95	510	28.14	910	52.88
		120	6.51	520	28.70	920	53.47
		130	7.07	530	29.26	930	54.06
		140	7.63	540	29.82	940	54.65
		150	8.19	550	30.39	950	55.25
		160	8.75	560	30.96	960	55.84
		170	9.31	570	31.53	970	56.43
		180	9.87	580	32.11	980	57.03
		190	10.43	590	32.69	990	57.63
-200	-8.27	200	10.99	600	33.27	1,000	58.22
-190	-8.02	210	11.56	610	33.86		
-180	-7.75	220	12.12	620	34.45		
-170	-7.46	230	12.68	630	35.04		
-160	-7.14	240	13.23	640	35.64		
-150	-6.80	250	13.79	650	36.24		
-140	-6.44	260	14.35	660	36.84		
-130	-6.06	270	14.90	670	37.45		
-120	-5.66	280	15.46	680	38.06		
-110	-5.25	290	16.01	690	38.68		
-100	-4.82	300	16.56	700	39.30		
-90	-4.38	310	17.12	710	39.93		
-80	-3.93	320	17.67	720	40.56		
-70	-3.47	330	18.22	730	41.19		
-60	-3.00	340	18.77	740	41.83		
-50	-2.52	350	19.32	750	42.48		
-40	-2.03	360	19.87	760	43.12		
-30	-1.53	370	20.42	770	43.77		
-20	-1.03	380	20.97	780	44.42		
-10	-0.52	390	21.52	790	45.07		
0	0.00	400	22.07	800	45.72		

<sup>1</sup> W. F. Roeser and A. I. Dahl, *J. Research Nat. Bur. Standards*, **20**, 337 (1938).

TABLE XIII  
IRON VS. CONSTANTAN THERMOCOUPLE<sup>1</sup>  
Degrees Fahrenheit, Reference Junction 32°F.

Temperature (°F.)	Electro- motive force (mv.)	Temperature (°F.)	Electro- motive force (mv.)	Temperature (°F.)	Electro- motive force (mv.)	Temperature (°F.)	Electro- motive force (mv.)	Temperature (°F.)	Electro- motive force (mv.)
		0	-0.92	500	14.35	1,000	29.70	1,500	46.74
		10	- .93	510	14.65	1,010	30.01	1,510	47.10
		20	- .35	520	14.96	1,020	30.33	1,520	47.47
		30	- .06	530	15.27	1,030	30.64	1,530	47.83
		40	+ .23	540	15.58	1,040	30.96	1,540	48.20
		50	.52	550	15.89	1,050	31.28	1,550	48.56
		60	.82	560	16.20	1,060	31.60	1,560	48.93
		70	1.11	570	16.50	1,070	31.92	1,570	49.29
		80	1.41	580	16.81	1,080	32.24	1,580	49.66
		90	1.70	590	17.12	1,090	32.56	1,590	50.02
		100	2.00	600	17.43	1,100	32.88	1,600	50.39
		110	2.30	610	17.73	1,110	33.20	1,610	50.75
		120	2.60	620	18.04	1,120	33.53	1,620	51.12
		130	2.90	630	18.34	1,130	33.86	1,630	51.49
		140	3.20	640	18.65	1,140	34.18	1,640	51.85
		150	3.50	650	18.95	1,150	34.51	1,650	52.22
		160	3.81	660	19.26	1,160	34.84	1,660	52.55
		170	4.11	670	19.56	1,170	35.17	1,670	52.88
		180	4.42	680	19.87	1,180	35.50	1,680	53.21
		190	4.72	690	20.18	1,190	35.84	1,690	53.54
-300	-7.87	200	5.03	700	20.48	1,200	36.17	1,700	53.87
-290	-7.72	210	5.34	710	20.79	1,210	36.50	1,710	54.20
-280	-7.55	220	5.64	720	21.09	1,220	36.84	1,720	54.52
-270	-7.38	230	5.95	730	21.40	1,230	37.18	1,730	54.85
-260	-7.20	240	6.26	740	21.70	1,240	37.52	1,740	55.18
-250	-7.02	250	6.57	750	22.01	1,250	37.86	1,750	55.51
-240	-6.83	260	6.88	760	22.31	1,260	38.20	1,760	55.84
-230	-6.63	270	7.19	770	22.62	1,270	38.54	1,770	56.17
-220	-6.43	280	7.50	780	22.92	1,280	38.88	1,780	56.50
-210	-6.22	290	7.81	790	23.23	1,290	39.23	1,790	56.83
-200	-6.01	300	8.12	800	23.53	1,300	39.58	1,800	57.16
-190	-5.79	310	8.43	810	23.84	1,310	39.93		
-180	-5.57	320	8.75	820	24.14	1,320	40.28		
-170	-5.34	330	9.06	830	24.45	1,330	40.63		
-160	-5.11	340	9.37	840	24.75	1,340	40.98		
-150	-4.87	350	9.68	850	25.06	1,350	41.34		
-140	-4.63	360	10.00	860	25.37	1,360	41.69		
-130	-4.38	370	10.31	870	25.67	1,370	42.05		
-120	-4.13	380	10.62	880	25.98	1,380	42.40		
-110	-3.88	390	10.93	890	26.29	1,390	42.76		
-100	-3.63	400	11.24	900	26.59	1,400	43.12		
-90	-3.37	410	11.56	910	26.90	1,410	43.48		
-80	-3.11	420	11.87	920	27.21	1,420	43.84		
-70	-2.85	430	12.18	930	27.52	1,430	44.20		
-60	-2.58	440	12.49	940	27.83	1,440	44.56		
-50	-2.31	450	12.80	950	28.14	1,450	44.92		
-40	-2.04	460	13.11	960	28.45	1,460	45.28		
-30	-1.76	470	13.42	970	28.76	1,470	45.65		
-20	-1.48	480	13.73	980	29.07	1,480	46.01		
-10	-1.20	490	14.04	990	29.39	1,490	46.37		
0	-0.92	500	14.35	1,000	29.70	1,500	46.74		

<sup>1</sup> W. F. Roeser and A. I. Dahl, *J. Research Nat. Bur. Standards*, **20**, 337 (1938).



TABLE XIV<sup>1</sup>

THERMAL E.M.F. OF IMPORTANT THERMOCOUPLE MATERIALS RELATIVE TO PLATINUM

Temp. (°C.)	Chromel P (mv.)	Alumel (mv.)	Copper (mv.)	Iron (mv.)	Constantan (mv.)
- 200	- 3.36	+ 2.39	- 0.19	- 2.92	+ 5.35
- 100	- 2.20	+ 1.29	- 0.37	- 1.84	+ 2.98
0	0	0	0	0	0
+ 100	+ 2.81	- 1.29	+ 0.76	+ 1.89	- 3.51
200	5.96	- 2.17	1.83	3.54	- 7.45
300	9.32	- 2.89	3.15	4.85	-11.71
400	12.75	- 3.64	4.68	5.88	-16.19
500	16.21	- 4.43	6.41	6.79	-20.79
600	19.62	- 5.28	8.34	7.80	-25.47
700	22.96	- 6.18	10.49	9.12	-30.18
800	26.23	- 7.08	12.84	10.86	-34.86
900	29.41	- 7.95	15.41	12.84	-39.45
1000	32.52	- 8.79	18.20	14.30	-43.92
1100	35.56	- 9.58			
1200	38.51	-10.34			
1300	41.35	-11.06			
1400	44.04	-11.77			

<sup>1</sup> *American Institute of Physics*, "Temperature—Its Measurement and Control in Science and Industry," New York, Reinhold Publishing Corp., 1941.

TABLE XV<sup>1</sup>  
THERMAL E.M.F. OF SOME ALLOYS RELATIVE TO PLATINUM

Temp. (°C.)	Man- ganin (mv.)	Gold- Chro- mium (mv.)	Copper- Beryl- lium (mv.)	Yellow brass (mv.)	Phosphor bronze (mv.)	Solder 50Sn- 50Pb (mv.)	Solder 96.5Sn- 3.5Ag (mv.)
0	0	0	0	0	0	0	0
+100	+0.61	-0.17	+0.67	+0.60	+0.55	+0.46	+0.45
200	1.55	-0.32	1.62	1.49	1.34		
300	2.77	-0.44	2.81	2.58	2.34		
400	4.25	-0.55	4.19	3.85	3.50		
500	5.95	-0.63	.....	5.30	4.81		
600	7.84	-0.66	.....	6.96	6.30		

Temp. (°C.)	18-8 Stainless steel (mv.)	Spring steel (mv.)	80Ni- 20Cr (mv.)	60Ni- 24Fe- 16Cr (mv.)	Copper coin (95Cu- 4Sn-1Zn) (mv.)	Nickel coin (75Cu- 25Ni) (mv.)	Silver coin (90Ag- 10Cu) (mv.)
0	0	0	0	0	0	0	0
+100	+0.44	+1.32	+1.14	+0.85	+0.60	-2.76	+0.80
200	1.04	2.63	2.62	2.01	1.48	-6.01	1.90
300	1.76	3.81	4.34	3.41	2.60	-9.71	3.25
400	2.60	4.84	6.25	5.00	3.91	-13.78	4.81
500	3.56	5.80	8.31	6.76	5.44	-18.10	
600	4.67	6.86	10.53	8.68	7.14	-22.59	8.64
700	5.93	.....	12.91	10.78			
800	7.37	.....	15.44	13.06			
900	8.99	.....	18.11	15.50			
1000	.....	.....	20.91	18.10			

<sup>1</sup> *American Institute of Physics*, "Temperature—Its Measurement and Control in Science and Industry," New York, Reinhold Publishing Corp., 1941.

TABLE XVI<sup>1</sup>ELECTRICAL RESISTIVITY AS A FUNCTION OF TEMPERATURE<sup>a</sup>[At 0°C. both the relative ( $R_t/R_0$ ) and actual resistivity (microhm-cm.) are given]

Temp. (°C)	Platinum ( $R_t/R_0$ )	Copper ( $R_t/R_0$ )	Nickel ( $R_t/R_0$ )	Iron ( $R_t/R_0$ )	Silver ( $R_t/R_0$ )	90 % Pt- 10 % Rh ( $R_t/R_0$ )	87 % Pt- 13 % Rh ( $R_t/R_0$ )
-200	0.177	0.117	.....	.....	0.176		
-100	0.599	0.557	.....	.....	0.596		
0	1.000 (9.83)	1.000 (1.56)	1.000 (6.38)	1.000 (8.57)	1.000 (1.50)	1.000 (18.4)	1.000 (19.0)
+100	1.892	1.431	1.663	1.650	1.408	1.166	1.156
200	1.773	1.862	2.501	2.464	1.827	1.330	1.308
300	2.142	2.299	3.611	3.485	2.256	1.490	1.456
400	2.499	2.747	4.847	4.716	2.698	1.646	1.601
500	2.844	3.210	5.398	6.162	3.150	1.798	1.744
600	3.178	3.695	5.882	7.839	3.616	1.947	1.885
700	3.500	4.208	6.327	9.790	4.094	2.093	2.023
800	3.810	4.752	6.751	12.009	4.586	2.234	2.157
900	4.109	5.334	7.156	12.790	5.091	2.370	2.287
1000	4.396	5.960	7.542	13.070	.....	2.503	2.414
1100	4.671	.....	.....	.....	.....	2.633	2.538
1200	4.935	.....	.....	.....	.....	2.761	2.660
1300	5.187	.....	.....	.....	.....	2.887	2.780
1400	5.427	.....	.....	.....	.....	3.011	2.898
1500	5.655	.....	.....	.....	.....	3.133	3.014

<sup>1</sup> *American Institute of Physics*, "Temperature—Its Measurement and Control in Science and Industry," New York, Reinhold Publishing Corp., 1941.

<sup>a</sup> The values below 0°C., in most cases, have not been determined on the same samples as the values above 0°C.

TABLE XVI.—(Continued)

Temp. (°C)	80Ni- 20Cr ( $R_t/R_o$ )	60Ni- 24Fe- 16Cr ( $R_t/R_o$ )	50Fe- 30Ni- 20Cr ( $R_t/R_o$ )	Chromel P (90Ni- 10Cr) ( $R_t/R_o$ )	Alumel 95Ni-Bal Al Si and Mn ( $R_t/R_o$ )	Constan- tan (55 Cu-45Ni) ( $R_t/R_o$ )	Manga- nin ( $R_t/R_o$ )
0	1.000 (107.6)	1.000 (111.6)	1.000 (99.0)	1.000 (70.0)	1.000 (28.1)	1.000 (48.9)	1.000 (48.2)
100	1.021	1.025	1.037	1.041	1.239	0.999	1.002
200	1.041	1.048	1.073	1.086	1.428	0.996	0.996
300	1.056	1.071	1.107	1.134	1.537	0.994	0.991
400	1.068	1.092	1.137	1.187	1.637	0.994	0.983
500	1.073	1.108	1.163	1.222	1.726	1.007	
600	1.071	1.115	1.185	1.248	1.814	1.024	
700	1.067	1.119	1.204	1.275	1.899	1.040	
800	1.066	1.127	1.221	1.304	1.982	1.056	
900	1.071	1.138	1.237	1.334	2.066	1.074	
1000	1.077	1.149	1.251	1.365	2.150	1.092	
1100	1.083	.....	.....	1.397	2.234	1.110	
1200	.....	.....	.....	1.430	2.318		

TABLE XVII  
SPECTRAL EMISSIVITY OF MATERIALS, SURFACE UNOXIDIZED

Element	$\epsilon_{0.65\mu}$		Element	$\epsilon_{0.65\mu}$	
	Solid	Liquid		Solid	Liquid
Beryllium.....	0.61	0.61	Thorium.....	0.36	0.40
Carbon.....	0.80-0.93		Titanium.....	0.63	0.65
Chromium.....	0.34	0.39	Tungsten.....	0.43	
Cobalt.....	0.36	0.37	Uranium.....	0.54	0.34
Columbium.....	0.37	0.40	Vanadium.....	0.35	0.32
Copper.....	0.10	0.15	Yttrium.....	0.35	0.35
Erbium.....	0.55	0.38	Zirconium.....	0.32	0.30
Gold.....	0.14	0.22	Steel.....	0.35	0.37
Iridium.....	0.30		Cast Iron.....	0.37	0.40
Iron.....	0.35	0.37	Constantan.....	0.35	
Manganese.....	0.59	0.59	Monel.....	0.37	
Molybdenum.....	0.37	0.40	Chromel P		
Nickel.....	0.36	0.37	(90Ni-10Cr)	0.35	
Palladium.....	0.33	0.37	80Ni-20Cr.....	0.35	
Platinum.....	0.30	0.38	60Ni-24Fe-16Cr....	0.36	
Rhodium.....	0.24	0.30	Alumel		
Silver.....	0.07	0.07	(95Ni; Bal. Al,		
Tantalum.....	0.49		Mn, Si)	0.37	
			90Pt-10Rh.....	0.27	

## TABLE XVIII

## SPECTRAL EMISSIVITY OF OXIDES

The emissivity of oxides and oxidized metals depends to a large extent upon the roughness of the surface. In general, higher values of emissivity are obtained on the rougher surfaces.

Material	$\epsilon_{0.65\mu}$ Range of observed values	$\epsilon_{0.65\mu}$ Probable value for the oxide formed on smooth metal
Aluminum oxide.....	0.22 to 0.40	0.30
Beryllium oxide.....	0.07 to 0.37	0.35
Cerium oxide.....	0.58 to 0.80	
Chromium oxide.....	0.60 to 0.80	0.70
Cobalt oxide.....		0.75
Columbium oxide.....	0.55 to 0.71	0.70
Copper oxide.....	0.60 to 0.80	0.70
Iron oxide.....	0.63 to 0.98	0.70
Magnesium oxide.....	0.10 to 0.43	0.20
Nickel oxide.....	0.85 to 0.96	0.90
Thorium oxide.....	0.20 to 0.57	0.50
Tin oxide.....	0.32 to 0.60	
Titanium oxide.....		0.50
Uranium oxide.....		0.30
Vanadium oxide.....		0.70
Yttrium oxide.....		0.60
Zirconium oxide.....	0.18 to 0.43	0.40
Alumel (oxidized).....		0.87
Cast Iron (oxidized).....		0.70
Chromel P (90Ni-10Cr) (oxidized)...		0.87
80Ni-20Cr (oxidized).....		0.90
60Ni-24Fe-16Cr (oxidized).....		0.83
55Fe-37.5Cr-7.5Al (oxidized).....		0.78
70Fe-23Cr-5Al-2Co (oxidized).....		0.75
Constantan (55Cu-45Ni) (oxidized)...		0.84
Carbon Steel (oxidized).....		0.80
Stainless Steel (18-8) (oxidized).....		0.85
Porcelain.....	0.25 to 0.50	

TABLE XIX  
TOTAL EMISSIVITY OF METALS, SURFACE UNOXIDIZED

Material	$\epsilon_t$					
	25°C.	100°C.	500°C.	1000°C.	1500°C.	2000°C.
Aluminum.....	0.022	0.028	0.060			
Bismuth.....	0.048	0.061				
Carbon.....	0.081	0.081	0.079			
Chromium.....		0.08				
Cobalt.....			0.13	0.23		
Columbium.....					0.19	0.24
				(Liquid		
Copper.....		0.02		0.15)		
Gold.....		0.02	0.03			
Iron.....		0.05				
Lead.....		0.05				
Mercury.....	0.10	0.12				
Molybdenum.....				0.13	0.19	0.24
Nickel.....	0.045	0.06	0.12	0.19		
Platinum.....	0.037	0.047	0.096	0.152	0.191	
Silver.....		0.02	0.035			
Tantalum.....					0.21	0.26
Tin.....	0.043	0.05				
Tungsten.....	0.024	0.032	0.071	0.15	0.23	0.28
Zinc.....	(0.05 at 300°C.)					
Brass.....	0.035	0.035				
Cast iron.....		0.21		(Liquid 0.29)		
Steel.....		0.08		(Liquid 0.28)		

TABLE XX

## TOTAL EMISSIVITY OF MISCELLANEOUS MATERIALS

(Most values are uncertain by 10% to 30%. In many cases value depends on particle size)

Material	Temp. (°C.)	$\epsilon_t$
Aluminum (oxidized).....	200 600	0.11 0.19
Brass (oxidized).....	200 600	0.61 0.59
Calorized copper.....	100 500	0.26 0.26
Calorized copper (oxidized).....	200 600	0.18 0.19
Calorized steel (oxidized).....	200 600	0.52 0.57
Cast iron (strongly oxidized).....	40 250	0.95 0.95
Cast iron (oxidized).....	200 600	0.64 0.78
Copper (oxidized).....	200 1000	0.6 0.6
Fire brick.....	1000	0.75
<sup>1</sup> Glass, smooth.....	20	.937
Gold enamel.....	100	0.37
<sup>1</sup> Hour frost (.1 to .2mm. thick).....	0	.985
Iron (oxidized).....	100 500 1200	0.74 0.84 0.89
Iron (rusted).....	25	0.65
Lead (oxidized).....	200	0.63
Monel (oxidized).....	200 600	0.43 0.43
Nickel (oxidized).....	200 1200	0.37 0.85
<sup>1</sup> Plaster, rough lime.....	10-90	.91
Silica brick.....	1000 1100	0.80 0.85
Steel (oxidized).....	25 200 600	0.80 0.79 0.79
Steel plate (rough).....	40 400	0.94 0.97
<sup>1</sup> Water.....	20	.965
<sup>1</sup> Wet ice.....	0	.966
Wrought iron (dull oxidized).....	25 350	0.94 0.94
20Ni-25Cr-55Fe (oxidized).....	200 500	0.90 0.97
60Ni-12Cr-28Fe (oxidized).....	270 560	0.89 0.82
80Ni-20C (oxidized).....	100 600 1300	0.87 0.87 0.89

<sup>1</sup> H. W. McAdams, *Heat Transmission*, Table I, "from Hottel." New York: McGraw-Hill, 1933, p. 383.



TABLE XXI

TRUE TEMPERATURES CORRESPONDING TO VARIOUS EMISSIVITIES AND  
 VARIOUS TEMPERATURES OBSERVED WITH AN OPTICAL PYROMETER  
 The Temperatures, in °C, are for  $\lambda = 0.65\mu$  and  $e_2 = 1.432$  cm. deg.

Spectral emis- sivity	Observed temperature in headings, true temperature in the body of the table										
	700	800	900	1000	1100	1200	1300	1400	1600	1800	2000
0.05	848	983	1123	1266	1415	1569	1728	1849	2240	2614	3017
0.10	810	935	1064	1195	1330	1468	1609	1754	2056	2373	2708
0.15	789	909	1032	1157	1284	1414	1546	1682	1960	2250	2552
0.20	774	891	1010	1130	1253	1378	1504	1633	1897	2170	2453
0.25	763	878	993	1111	1230	1350	1473	1597	1850	2111	2379
0.30	755	867	980	1095	1211	1329	1448	1568	1814	2065	2322
0.35	747	858	969	1082	1196	1311	1427	1545	1783	2027	2276
0.40	741	850	960	1071	1183	1296	1410	1525	1758	1996	2237
0.45	736	843	952	1062	1172	1283	1395	1508	1736	1968	2204
0.50	731	837	945	1053	1162	1272	1382	1493	1717	1945	2175
0.55	726	832	939	1046	1153	1261	1370	1480	1700	1923	2149
0.60	722	827	933	1039	1145	1252	1360	1467	1685	1905	2126
0.65	719	823	927	1032	1138	1244	1350	1457	1671	1888	2106
0.70	716	819	923	1027	1131	1236	1341	1447	1659	1872	2087
0.75	712	815	917	1021	1125	1229	1333	1437	1647	1858	2069
0.80	710	812	914	1017	1119	1222	1325	1429	1636	1844	2054
0.85	707	809	910	1012	1114	1216	1318	1421	1626	1832	2039
0.90	704	805	907	1008	1109	1210	1312	1413	1617	1821	2025
0.95	702	803	903	1004	1104	1205	1306	1407	1608	1810	2012
1.00	700	800	900	1000	1100	1200	1300	1400	1600	1800	2000

TABLE XXI

TRUE TEMPERATURES CORRESPONDING TO VARIOUS VALUES OF TOTAL  
EMISSIVITY AND VARIOUS BRIGHTNESS TEMPERATURES  
(All temperatures in °C.)

Total emis- sivity	Observed temperature in headings, true temperature in body of table										
	100	200	300	400	600	800	1000	1200	1400	1600	1800
0.05	422	686	916	1137	1567	1993	2317	2841	3264	3687	4110
0.10	316	536	728	913	1275	1632	1989	2345	2701	3057	3413
0.15	264	460	633	799	1126	1449	1771	2093	2415	2736	3058
0.20	231	410	571	725	1029	1330	1629	1929	2228	2527	2827
0.25	207	375	526	672	958	1243	1526	1809	2093	2376	2658
0.30	189	347	491	630	904	1175	1446	1717	1987	2258	2528
0.35	175	325	463	596	860	1121	1381	1642	1902	2162	2422
0.40	164	307	439	568	823	1075	1327	1579	1830	2082	2333
0.45	154	291	419	544	791	1036	1281	1525	1769	2014	2258
0.50	146	278	402	523	763	1002	1240	1478	1716	1954	2192
0.55	138	266	387	505	739	972	1204	1437	1669	1902	2134
0.60	132	255	373	489	718	945	1173	1400	1628	1855	2082
0.65	126	246	361	474	698	921	1144	1367	1590	1813	2036
0.70	121	238	350	461	680	900	1119	1337	1556	1775	1993
0.75	117	230	340	448	664	880	1095	1310	1525	1740	1955
0.80	113	223	331	437	649	861	1073	1284	1496	1707	1919
0.85	109	217	322	427	636	844	1053	1261	1469	1678	1886
0.90	106	211	314	417	623	828	1034	1239	1445	1650	1855
0.95	103	205	307	408	611	814	1016	1219	1422	1624	1827
1.00	100	200	300	400	600	800	1000	1200	1400	1600	1800

TABLE XXII

## PROPERTIES OF TUNGSTEN

(The values of  $\epsilon_c$ ,  $T_c$ , and  $T_{0.65\mu}$  have been calculated from the spectral emissivities  $\epsilon_{0.65\mu}$  and  $\epsilon_{0.467\mu}$ )

True temperature ( $T$ °K.)	Relative resistance ( $R_T/R_{273}$ )	Normal brightness (New candles per cm. <sup>2</sup> )	Spectral emissivity		Color emissivity ( $\epsilon_c$ )	Total emissivity $\epsilon_t$	Brightness temperature $T_{0.65\mu}$	Color temperature $T_c$
			$\epsilon_{0.65\mu}$	$\epsilon_{0.467\mu}$				
300	1.12	.....	0.472	0.505	.....	0.032		
400	1.58	.....			.....	.042		
500	2.07	.....			.....	.053		
600	2.58	.....			.....	.064		
700	3.11	.....			.....	.076		
800	3.65	.....			.....	.088		
900	4.21	.....			.....	.101		
1000	4.78	0.0001	.458	.486	0.395	.114	966	1007
1100	5.36	0.001	.456	.484	.392	.128	1059	1108
1200	5.95	0.006	.454	.482	.390	.143	1151	1210
1300	6.55	0.029	.452	.480	.387	.158	1242	1312
1400	7.16	0.11	.450	.478	.385	.175	1332	1414
1500	7.78	0.33	.448	.476	.382	.192	1422	1516
1600	8.41	0.92	.446	.475	.380	.207	1511	1619
1700	9.04	2.3	.444	.473	.377	.222	1599	1722
1800	9.69	5.1	.442	.472	.374	.236	1687	1825
1900	10.34	10.4	.440	.470	.371	.249	1774	1928
2000	11.00	20.0	.438	.469	.368	.260	1861	2032
2100	11.65	36	.436	.467	.365	.270	1946	2136
2200	12.33	61	.434	.466	.362	.279	2031	2241
2300	13.01	101	.432	.464	.359	.288	2115	2345
2400	13.69	157	.430	.463	.356	.296	2198	2451
2500	14.38	240	.428	.462	.353	.303	2280	2556
2600	15.08	350	.426	.460	.349	.311	2362	2662
2700	15.78	500	.424	.459	.346	.318	2443	2769
2800	16.48	690	.422	.458	.343	.323	2523	2876
2900	17.19	950	.420	.456	.340	.329	2602	2984
3000	17.90	1260	.418	.455	.336	.334	2681	3092
3100	18.62	1650	.416	.454	.333	.337	2759	3200
3200	19.35	2100	.414	.452	.330	.341	2837	3310
3300	20.08	2700	.412	.451	.326	.344	2913	3420
3400	20.82	3400	.410	.450	.323	.348	2989	3530
3500	21.56	4200	.408	.449	.320	.351	3063	3642
3600	22.30	5200	.406	.447	.317	.354	3127	3754

TABLE XXIII

RELATIVE HUMIDITY FROM WET- AND DRY-BULB THERMOMETER READINGS  
IN STILL AIR

Calculated for a barometer height of 755 mm. At altitudes of 6,000 feet or over the reduction in barometric pressure will cause an error of 5 per cent or over at very low humidities.

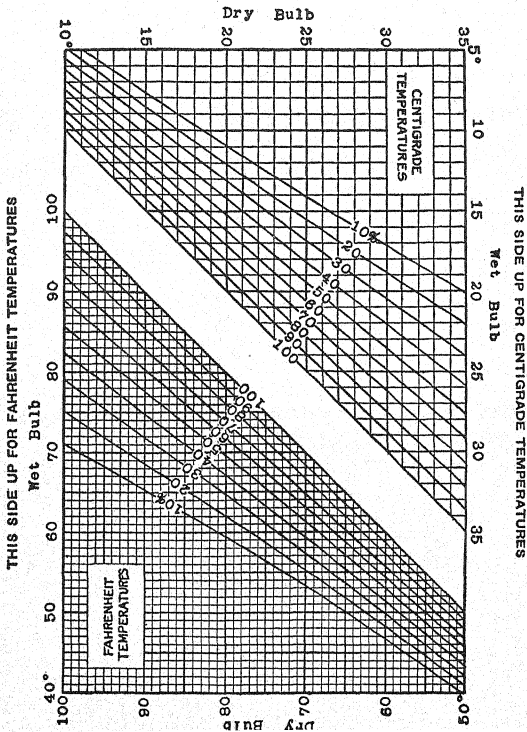


TABLE XXIV  
PRESSURE OF SATURATED WATER VAPOR  
*T* in deg C.; *P* in mm. Hg

<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>
-10	2.149	13	11.231	36	44.563	59	142.60	82	384.9	105	906.07	128	1907.83
-9	2.326	14	11.987	37	47.067	60	149.38	83	400.6	106	937.92	129	1966.35
-8	2.514	15	12.788	38	49.692	61	156.43	84	416.8	107	970.60	130	2026.16
-7	2.715	16	13.634	39	52.442	62	163.77	85	433.6	108	1004.42	131	2087.42
-6	2.931	17	14.530	40	55.324	63	171.38	86	450.9	109	1038.92	132	2150.42
-5	3.163	18	15.477	41	58.34	64	179.31	87	468.7	110	1074.56	133	2214.64
-4	3.410	19	16.477	42	61.50	65	187.54	88	487.1	111	1111.20	134	2280.76
-3	3.673	20	17.535	43	64.80	66	196.09	89	506.1	112	1148.74	135	2347.26
-2	3.956	21	18.650	44	68.26	67	204.96	90	525.76	113	1187.42	136	2416.34
-1	4.258	22	19.827	45	71.88	68	214.17	91	546.05	114	1227.25	137	2488.16
0	4.579	23	21.068	46	75.65	69	223.73	92	566.99	115	1267.98	138	2560.67
1	4.926	24	22.377	47	79.60	70	233.7	93	588.60	116	1309.94	139	2634.84
2	5.294	25	23.756	48	83.71	71	243.9	94	610.90	117	1352.95	140	2710.92
3	5.685	26	25.209	49	88.02	72	254.6	95	633.90	118	1397.18	141	2788.44
4	6.101	27	26.739	50	92.51	73	265.7	96	657.62	119	1442.63	142	2867.48
5	6.543	28	28.349	51	97.20	74	277.2	97	682.07	120	1489.14	143	2948.80
6	7.013	29	30.043	52	102.09	75	289.1	98	707.27	121	1536.80	144	3031.64
7	7.513	30	31.824	53	107.20	76	301.4	99	733.24	122	1586.04	145	3116.76
8	8.045	31	33.695	54	112.51	77	314.1	100	760.00	123	1636.36	146	3203.40
9	8.609	32	35.663	55	118.04	78	327.3	101	787.51	124	1687.81	147	3292.32
10	9.209	33	37.729	56	123.80	79	341.0	102	815.86	125	1740.03	148	3282.76
11	9.844	34	39.898	57	129.82	80	355.1	103	845.12	126	1795.12	149	3476.24
12	10.518	35	42.175	58	136.08	81	369.7	104	875.06	127	1850.83	150	3570.48
				160	4636.00	180	7520.20	200	11659.16				
				170	5940.92	190	9413.36						

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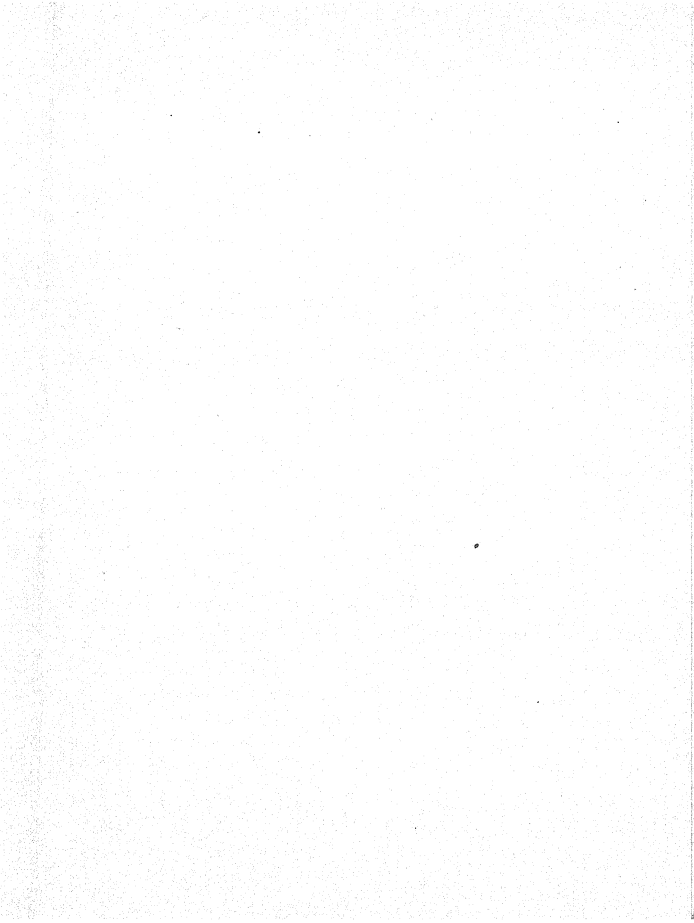


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